

DISSERTATION

PART 1: EXCITED ELECTRONIC STATE DECOMPOSITION
OF ENERGETIC MOLECULES

PART 2: CONFORMATION SPECIFIC REACTIVITY OF RADICAL CATION
INTERMEDIATES OF BIOACTIVE MOLECULES

Submitted by

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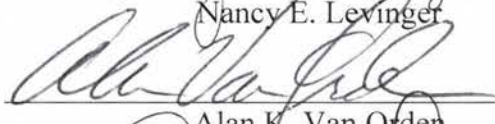
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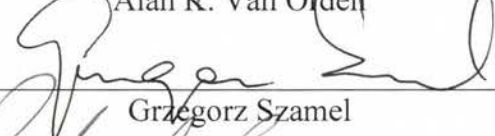
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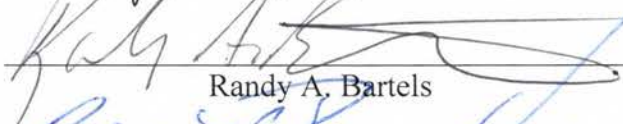
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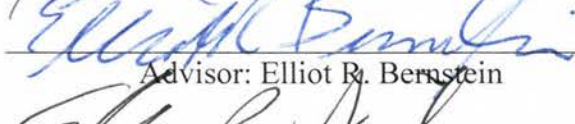
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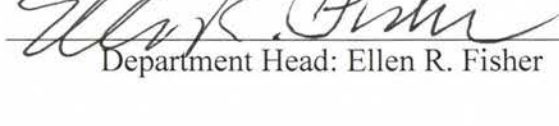
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ABSTRACT OF DISSERTATION

PART 1: EXCITED ELECTRONIC STATE DECOMPOSITION OF ENERGETIC MOLECULES

Energetic materials have a wide variety of industrial, civil, and military applications. They include a number of organic compounds such as RDX (1,3,5-trinitroheahydro-s-triazine), HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine), DAAF (3,3'-diamino-4,4'-azoxyfurazan), DAATO_{3.5} (3,3'-azobis(6-amino-1,2,4,5-tetrazine)-mixed N-oxides), etc. These materials release huge chemical energy during their decomposition. The decomposition of energetic materials is initiated with a shock or compression wave or a spark. Such events in solids generate molecules in the excited electronic states. Hence, in order to maximize release of the stored chemical energy in the most efficient and useful manner and to design new energetic materials, the unimolecular decomposition mechanisms and dynamics from excited electronic states should be understood for these systems. This thesis describes understanding about unimolecular decomposition of energetic materials from their excited electronic states. A few fundamental questions at molecular level dealing with electronic excitation of energetic materials are addressed here: (a) what happens immediately after electronic excitation of energetic molecules?; (b) how is excess energy partitioned among product molecules following electronic excitation?; (b) what are the mechanism and dynamics

of molecular decomposition?; (d) does nonadiabatic chemistry (a process that span multiple electronic potential energy surfaces) through conical intersection (crossing of different potential energy surfaces) dominate system behavior?

Both energy and time resolved spectroscopic techniques are used in this effort. The product internal state (rotational and vibrational) distributions are probed using mass and energy resolved spectroscopic techniques using time-of-flight mass spectrometry (TOFMS) and laser induced fluorescence (LIF) spectroscopy. Analyzing the product internal state distributions, the mechanisms of unimolecular decomposition of energetic molecules from excited electronic states are determined. The femtosecond pump-probe spectroscopic technique is utilized to determine ultrafast decomposition dynamics of these molecules. From a theoretical point of view, multiconfigurational methodologies such as, CASSCF and CASMP2 are used to model the processes involving excited electronic states of energetic molecules. Influence of nonadiabatic chemistry in the overall decomposition of energetic molecules is also theoretically judged.

The primary energetic systems whose nonadiabatic chemistry discussed here are the nitramine (e.g., RDX, HMX), furazan (e.g., DAAF), and tetrazine-N-oxide (e.g., DAATO_{3.5}) based energetic species. A number of model systems, which are simple analogue molecules of the large and more complex energetic materials, are studied in detail to understand nonadiabatic energetic behavior of a single energetic moiety of particular class. Subsequently, the decomposition mechanism for more complex energetic systems are studied and compared with that of their model systems. Nitramine energetic materials and model systems undergo nitro-nitrite isomerization followed by

NO elimination. Nitramine energetic materials dissociates in the ground state generating rotationally cold (20 K) distribution of the NO product. Nitramine model systems dissociates in the excited state surface producing rotationally hot (~120 K) distribution of the NO product. The nitro-nitrite isomerization happens through conical intersection. Furazan based model molecules (e.g., furazan) possess two different pathways of decomposition: ring contraction and ring opening. These two pathways are electronically nonadiabatic. The ring contraction mechanism generates rotationally cold (20 K) product NO and the ring opening mechanism generates rotationally hot (100 K) product NO. Furazan based energetic material (DAAF), however, dissociates only through a ring contraction mechanism. Thus nonadiabatic pathways control the decomposition of furazan based molecules. Decomposition of tetrazine-2,4-dioxide based molecules involves a ring contraction mechanism through $(S_1/S_0)_{CI}$, producing only rotationally cold (20 K) but vibrationally hot (1200 K) distributions of the NO product. Tetrazine-1,4-dioxide undergoes similar decomposition pathway through $(S_1/S_0)_{CI}$; however, it produces rotationally hotter (50 K) but vibrationally colder distribution of the NO product. Thus the relative position of the oxygen atoms attached to the tetrazine ring is important parameter along with their nonadiabatic chemistry controlling their final energetic reactivity. Decomposition dynamics of all energetic materials is faster than 180 fs. Considering the influence of conical intersections in the excited electronic state decomposition of energetic materials, rotationally cold N_2 product is predicted to be the major decomposition product of high nitrogen content energetic species.

The present work infers that generation of internally cold product is an important characteristics of a true energetic molecule. Presence of low lying chemically relevant conical intersections provides a direct pathway of ultrafast decomposition chemistry of energetic molecules. The energy barrier to the low lying chemically relevant conical intersection, in principle, would be a point of interest to make a system more or less energetic.

PART 2: CONFORMATION SPECIFIC REACTIVITY OF RADICAL CATION INTERMEDIATES OF BIOACTIVE MOLECULES

Molecular Conformation plays an important role in biochemical reactions. Molecular conformers can interconvert via hindered rotations about single bonds. Quantum mechanical description of conformations infers that they are located at different positions on potential energy surface (PES). If different conformers are subjected to a biochemical reaction they may undergo different reactions from these distinct regions of PES and product selectivity can be seen in the conformation specific reaction.

Biomolecules such as amino acids and proteins provides a great conformational diversity because of their flexible structures. When conformers of biomolecules are subjected to biological reactions, the fate of the reactions can be expected to be heavily destined by their detailed molecular structures at the beginning of the reactions. Therefore, understanding relationship between conformers and biochemical reactivity

of the flexible biomolecules is essential for understanding and control of biological reactions.

Part 2 of this thesis discusses about conformation specific reactivity of radical cation intermediates of biomolecules. The radical cation intermediates are generated by means of removal of an electron from the parent biomolecules due to the effect of ionizing radiation, oxidative stress, and metal cofactors, which finally causes extensive damage to amino acids, peptides, and living body. Therefore, a detailed conformation specific characterization of the reactivity and stability of radical cationic bioactive species is highly desirable.

In this effort, first, conformation specific radical cation intermediate chemistry of α -substituted (amino, hydroxy, and keto) bioactive carboxylic acids is discussed. Finally, folding specific reactivity of small peptide analogues is addressed. The reactivity of radical cation carboxylic acids and peptide analogue molecule is investigated on the basis of mass spectrometry, infrared-vacuum ultraviolet (IR-VUV) photoionization spectroscopy, and high-level correlated *ab initio* calculations. Their reactivity is found to be highly conformation specific and is governed by their initial charge distribution following ionization. In the present work, the radical cations of lactic acid, pyruvic acid, glycine, valine, and a peptide analogue $\text{CH}_3\text{CO-Gly-NH}_2$ are studied to probe their stability and conformation specific reactivity following single photon, vertical ionization at 10.5 eV. For lactic acid, glycine, and valine, the localization site of the hole following sudden removal of an electron depends on their specific intramolecular hydrogen bonding network. Folding/turn specific dissociation of radical cationic peptide analogue $\text{CH}_3\text{CO-Gly-NH}_2$ is also predicted. Thus, the present

study reveals that the specific conformations of biomolecules govern their radical cationic reactivity.

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Shortly after I began working with Elliot, I focused on theoretical calculations on energetic molecules. During this time, the encouragement and help I have obtained from an excellent graduate student, Elena was priceless. At the same time, I focused on leaning experiments from two very talented coworkers, Yuanqing and Margo. Later on, Yuanqing has been a tremendous experimental resource for me during my graduate study. He quite possibly knows everything that needs to be done when a laser system is

malfunctioning. Yuanqing and I worked together on a majority of the experiments that make up the energetic material research work presented in this thesis. Working with him has been fun and fruitful. I would like to show my hearty gratitude to him for teaching me the experimental details, proof-reading my papers and thesis, and giving me suggestions in designing experiments and analyzing experimental results.

In the middle of my journey, I took interest in studying biological systems in gas phase. For this study, I learned the IR-VUV technique from another two talented coworkers Joong-Won and Keven. I am indebted to Joong-Won for letting me bug him repeatedly with questions about OPO systems. He showed me how to record IR-VUV spectrum of methanol and taught me many things about General valve. Keven was always willing to drop what he was doing to help me with my calculations of ion states of amino acids. I would like to thank him for providing me the optimized valine conformers and drawing my attention to their correct stability order.

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FOR SONU

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Part 1: Excited Electronic State Decomposition of Energetic Molecules

CHAPTER 1

Introduction

Excited Electronic State Decomposition of Energetic Molecules

1.1 Overview

Energetic materials are controllable storage systems of chemical energy. They have a wide variety of industrial, civil, and military applications. They encompass different classes of chemical compositions of fuels, explosives, propellants, and pyrotechniques. Distinctions among the classes are characterized usually in terms of the types of products generated, the magnitude of adiabatic exotherm, and the rate of decomposition reactions. Energetic materials decompose rapidly upon initiation and release large quantities of energy.

The research field of energetic materials has long been considered primarily for its practical aspects involving synthesis and assessing performance. In order to understand the combustion of energetic materials fully, to maximize release of the chemically stored energy from these materials in the most efficient and useful manner, and to design new energetic materials, however, the details of the chemistry and physics of the decomposition of energetic materials must certainly be understood.¹ Furthermore, the nature of the individual reaction steps, the dynamics of the dissociation, and the energy released during combustion reactions of energetic materials must be recognized.

The process of understanding the decomposition of energetic materials must begin with an exploration of their unimolecular behavior. Issues of interest in this area include elucidation of the initial unimolecular decomposition reaction steps, the dynamics of the dissociation, energy localization in the molecule, and release of energy from the molecule during the decomposition reaction. Such detailed information at the microscopic level may be used directly or as an input for molecular dynamics simulations to gain insight for condensed phase processes. If certain key unimolecular steps can be identified, one can in principle make a material less or more sensitive or “energetic” by some chemical modification that raises or lowers the activation energy barriers for specific steps in the decomposition process.

Decomposition of energetic materials is an extremely complex process in which numerous chemical and physical events occur in a concerted or step-wise fashion, and whose reaction mechanisms are strongly dependent on a wide variety of factors. The focus of this thesis is on identifying mechanisms and measuring the dynamics of key unimolecular decomposition reaction steps for different energetic materials, investigating factors which control the energy release, and experimental and theoretical challenges involved in their unimolecular decomposition study.

Decomposition of energetic materials can be initiated with a shock or compression wave. Experimental evidence indicates that electronic excitation (electrons, holes, excitons) plays a key role in the initiation process.²⁻⁹ Williams was the first to consider the influence of electronic states and electronic transport on the initiation and propagation of detonation waves in solid explosives.¹⁰ Dremin *et al.*, noting evidence of similarities between shock decomposition intermediates and those of

photochemical processes, proposed electronic excitation as the first molecular response in their multiprocess detonation model.¹¹ They postulate that detonation is caused by dissociation of molecules within the shock front, which can proceed in three ways: through the accumulation mechanism,^{12,13} through thermal ionization, and finally by electronic excitation.¹⁴ The lowest singlet–triplet excitations in the model gas-phase energetic molecules were investigated.¹⁵ Furthermore, correlation of impact sensitivity with electronic levels of a homologous series of explosive compounds has been reported.¹⁶ Finally, Gillman^{17,18} proposed that the compression from the wave front causes local metallization, which in turn causes bending of covalent bonds, and thus decreases the HOMO–LUMO gap and that sensitivity correlates with the formation of delocalized electrons. It was also suggested that plasmon excitation may trigger fast chemical reactions in a shock front.¹⁹ The idea of the involvement of excited electronic states was further buttressed by studies on RDX ($C_3H_6N_6O_6$) and TATB ($C_6H_6N_6O_6$), among other systems, in which initiation sensitivity was found to correlate with details of the electronic structure.^{20,21} The relationship between the defect structure, electronic excitations, and chemical processes under shock conditions in the detonation front is established by Kuklja et al.²² Therefore, electronically excited states play an important role in the initial step of decomposition of energetic materials and elucidation of detailed fundamental steps in the unimolecular decomposition of energetic molecules from their low lying excited electronic states is essential for understanding, controlling, and enhancing the detonation performances of these materials.²³

From an experimental point of view, energy resolved and time resolved spectroscopic techniques are used to explore the mechanism and dynamics of excited

electronic state decomposition of energetic materials. The forces or torques that act on the departing fragments during dissociation of a parent molecule give rise to clear fingerprints in product internal state (rotational and vibrational) energy distributions. The internal energy/state distributions of the products generated following electronic excitation of the parent molecules are probed using mass and energy resolved spectroscopic techniques utilizing either time of flight mass spectrometry (TOFMS) or laser induced fluorescence (LIF) spectroscopy. Knowledge of internal energy distributions of the product molecules ultimately leads to determination of decomposition mechanism of energetic materials. Dynamics of the decomposition reaction is determined by femtosecond pump-probe spectroscopy. Utilizing energy resolved and time resolved techniques, the mechanism and dynamics of unimolecular decomposition of energetic molecules are examined.

From a theoretical point of view, multiconfigurational methodologies are used to model excited electronic state decomposition of energetic materials. Involvement of excited electronic states in the initial step of the decomposition of energetic molecules undoubtedly infers that the specific topology of the excited electronic potential energy surfaces (PESs) will determine and control the unimolecular decomposition steps of these materials. In recent years, extensive work on photophysical and photochemical processes of organic polyatomic molecules has firmly established that conical intersections which arise due to the crossing of multidimensional electronic PESs play an important role in processes involving excited electronic states.²⁴ One of the most important implications of the presence of conical intersections is to allow extremely fast and efficient internal conversion of a molecule from upper to the lower electronic

states. Therefore, conical intersections allow nonadiabatic chemistry (a chemical process in which more than one PES is involved) to occur. This thesis presents a number of novel ideas concerning nonadiabatic molecular chemistry of energetic materials through conical intersections to provide theoretical model of and background for the experimental observations.

Thus results presented in this thesis show that synergism between experiment and theory can lead to greater understanding of the decomposition mechanisms and dynamics of energetic materials, and how nonadiabatic chemistry and physics plays a role in the initial steps of decomposition of energetic materials. In a broader context, the results presented in this thesis raise a few fundamental questions: can we predict explosive or energetic behavior relying on possible pathways of their nonadiabatic processes; do conical intersections always have relevance for the excited electronic state decomposition of energetic materials; and why are some molecules energetic and some structurally similar ones not energetic?

The primary energetic systems, whose excited electronic state decomposition are discussed in this thesis, are nitro-containing, nitramine, furazan, and tetrazine-N-oxide based energetic species. Excited electronic state decomposition of a number of model systems, which are simple analogue molecules of the larger and more complex energetic species, are also addressed in this work to provide detailed information on the decomposition behavior of the energetic moieties of particular class. Subsequently, the decomposition mechanism for more complex energetic systems are presented and compared with that of their model systems.

The format of the Part 1 of this thesis is as follows: the second chapter addresses decomposition behavior of a simple analogue molecule of nitramine energetic materials, dimethylnitramine ((CH₃)₂NNO₂). Decomposition of nitramine energetic materials is presented previously in Dr. Margo Greenfield's thesis.²⁵ The third chapter addresses decomposition dynamics of nitromethane (CH₃NO₂). The fourth chapter discusses decomposition behavior of furazan based energetic molecules. The fifth chapter discusses decomposition behavior of tetrazine-N-oxide based energetic systems. The sixth chapter presents nonadiabatic chemistry of different classes of energetic materials and model systems. The seventh chapter focuses on unfinished work and future directions of the energetic materials research. The eighth chapter addresses general conclusion on decomposition of energetic materials.

1.2 Summary of Decomposition of Important Energetic Molecules

The Initial Steps in the Decomposition of a Model Nitramine Energetic Material: Dimethylnitramine²⁶

Decomposition of dimethylnitramine (DMNA, (CH₃)₂NNO₂) has been studied extensively over the past decades. Although several different mechanisms have been proposed for the initial decomposition of DMNA, the dominant decomposition channel is still far from fully understood. All the results reported in the literature, along with our new experimental and theoretical results, are collected into a single reference for a sensible comparison in order to reach a general conclusion on DMNA decomposition. In this effort, nanosecond laser, energy resolved spectroscopy and complete active space self-consistent field (CASSCF) calculations are employed. The parent DMNA molecule is electronically excited using two different UV excitation wavelengths, 226 and 193 nm, to initiate the decomposition process. The NO molecule is observed as a

major decomposition product with relatively hot (120 K) rotational and cold vibrational distributions by both time-of-flight mass spectrometry and laser induced fluorescence spectroscopy. Based on the experimental observations, a nitro-nitrite isomerization mechanism is predicted to be the major channel of decomposition of DMNA in the excited electronic state with a minor contribution from the HONO elimination mechanism. The branching ratio between nitro-nitrite isomerization and HONO elimination channels is estimated to be approximately 1:0.04. CASSCF calculations show that surface crossing (conical intersection) between upper and lower electronic states along the nitro-nitrite isomerization reaction coordinate plays an important role in the overall decomposition of DMNA. Presence of such an (S_2/S_1)_{CI} conical intersection in the nitro-nitrite isomerization reaction coordinate provides a direct nonadiabatic decomposition pathway from the Franck Condon (FC) point of the S_2 surface which is experimentally accessed by 226 nm photoexcitation. This excited state isomerization takes place through a loose geometry for which the NO₂ moiety interacts with the (CH₃)₂N moiety from a long distance (~2.8 Å); however, in the ground electronic state, a similar (S_1/S_0)_{CI} conical intersection in this nitro-nitrite isomerization reaction coordinate hinders the isomerization exit channel, rendering NO₂ elimination as the major thermal decomposition channel of DMNA.

Photodissociation Dynamics of Nitromethane at 226 and 271 nm at Both Nanosecond and Femtosecond Time Scales²⁷

Photodissociation of nitromethane has been investigated for decades both theoretically and experimentally; however, as a whole picture, the dissociation dynamics for nitromethane are still not clear, although many different mechanisms have been proposed. In order to make a complete interpretation of these different

mechanisms, photolysis of nitromethane at 226 and 271 nm under both collisional and collisionless conditions is investigated at nanosecond and femtosecond time scales. These two laser wavelengths correspond to the $\pi^* \leftarrow \pi$ and $\pi^* \leftarrow n$ excitations of nitromethane, respectively. In nanosecond 226 nm ($\pi^* \leftarrow \pi$) photolysis experiments, CH_3 and NO radicals are observed as major products employing resonance enhanced multiphoton ionization techniques and time of flight mass spectrometry. Additionally, OH and CH_3O radicals are weakly observed as dissociation products employing laser induced fluorescence spectroscopy; the CH_3O product is only observed under collisional conditions. In femtosecond 226 nm experiments, CH_3 , NO_2 , and NO products are observed. These results confirm that rupture of the C-N bond should be the main primary process for the photolysis of nitromethane after the $\pi^* \leftarrow \pi$ excitation at 226 nm, and the NO_2 molecule should be the precursor of the observed NO product. Formation of the CH_3O radical after the recombination of CH_3 and NO_2 species under collisional conditions rules out a nitro-nitrite isomerization mechanism for the generation of CH_3O and NO from $(\pi\pi^*) \text{CH}_3\text{NO}_2$. The OH radical formation for $(\pi\pi^*) \text{CH}_3\text{NO}_2$ should be a minor dissociation channel because of the weak OH signal in both nanosecond and femtosecond (non-observable) experiments. Single color femtosecond pump-probe experiments at 226 nm are also employed to monitor the dynamics of the dissociation of nitromethane after the $\pi^* \leftarrow \pi$ excitation. Due to the ultrafast dynamics of product formation at 226 nm, the pump-probe transients for the three dissociation products are measured as an autocorrelation of the laser pulse, indicating the dissociation of nitromethane in the $(\pi\pi^*)$ excited state is faster than the laser pulse duration (180 fs). In nanosecond 271 nm ($\pi^* \leftarrow n$) photolysis experiments, pump-probe

experiments are performed to detect potential dissociation products, such as CH_3 , NO_2 , CH_3O and OH ; however, none of them is observed. In femtosecond 271 nm laser experiments, the nitromethane parent ion is observed with major intensity, together with CH_3 , NO_2 and NO fragment ions with only minor intensity. Pump-probe transients for both nitromethane parent and fragment ions at 271 nm excitation and 406.5 nm ionization display a fast exponential decay with a constant time of 36 fs, which we suggest to be the lifetime of the excited ($n\pi^*$) state of nitromethane. Combined with the 271 nm nanosecond pump-probe experiments, in which none of the CH_3 , NO_2 , CH_3O or OH fragment is observed, we suggest that all the fragment ions generated in 271 nm femtosecond laser experiments are derived from the parent ion, and dissociation of nitromethane from the ($n\pi^*$) excited electronic state does not occur in a supersonic molecular beam under collisionless conditions.

Excited Electronic State Decomposition of Furazan Based Energetic Materials: 3,3'-diamino-4,4'-azoxyfurazan (DAAF) and its Model Systems, Diaminofurazan (DAF) and Furazan²⁸

This work reports the first experimental and theoretical study of gas phase excited electronic state decomposition of a furazan based, high nitrogen content energetic material, 3,3'-diamino-4,4'-azoxyfurazan (DAAF) and its model systems, diaminofurazan (DAF) and furazan ($\text{C}_2\text{H}_2\text{N}_2\text{O}$). DAAF has received major attention as an insensitive high energy explosive; however, the mechanism and dynamics of the decomposition of this material is not clear yet. In order to understand the initial decomposition mechanism of DAAF and its model systems, ns energy resolved and fs time resolved spectroscopies, and complete active space self-consistent field (CASSCF) calculations have been employed to investigate the excited electronic state

decomposition of these materials. The NO molecule is observed as an initial decomposition product from DAAF and its model systems at three UV excitation wavelengths (226 nm, 236 nm, and 248 nm) with a pulse duration of 8 ns. Energies of the three excitation wavelengths coincide with the (0-0), (0-1) and (0-2) vibronic bands of the NO $A^2\Sigma^+ \leftarrow X^2\Pi$ electronic transition, respectively. A unique excitation wavelength independent dissociation channel is observed for DAAF, which generates the NO product with a rotationally cold (20 K) and a vibrationally hot (1265 K) distribution. On the contrary, excitation wavelength dependent dissociation channels are observed for the model systems, which generate the NO product with both rotationally cold and hot distributions depending on the excitation wavelengths. Potential energy surface calculations at the CASSCF level of theory illustrate that two conical intersections between the excited and ground electronic states are involved in two different, excitation wavelength dependent, dissociation channels for the model systems. Fs pump-probe experiments at 226 nm reveal that the NO molecule is still the main observed decomposition product from the materials of interest, and that the formation dynamics of the NO product is faster than 180 fs. Two additional fragments are observed from furazan with mass of 40 amu (C_2H_2N) and 28 amu (CH_2N) employing fs laser ionization. This observation suggests a five-membered heterocyclic furazan ring opening mechanism with rupture of a CN and an NO bond, yielding NO as a major decomposition product. NH_2 is not observed as a secondary decomposition product of DAAF and DAF.

Unimolecular Decomposition of Tetrazine-N-oxide Based High Nitrogen Content Energetic Materials from Excited Electronic States²⁹

Unimolecular excited electronic state decomposition of novel high nitrogen content energetic molecules, such as 3,3'-azobis(6-amino-1,2,4,5-tetrazine)-mixed N-oxides (DAATO_{3.5}), 3-amino-6-chloro-1,2,4,5-tetrazine-2,4-dioxide (ACTO), and 3,6-diamino-1,2,4,5-tetrazine-1,4-dioxide (DATO), is investigated. Although these molecules are based on N-oxides of a tetrazine aromatic heterocyclic ring, their decomposition behavior distinctly differs from that of bare tetrazine, in which N₂ and HCN are produced as decomposition products through a concerted dissociation mechanism. NO is observed to be an initial decomposition product from all tetrazine-N-oxide based molecules from their low lying excited electronic states. The NO product from DAATO_{3.5} and ACTO is rotationally cold (20 K) and vibrationally hot (1200 K), while the NO product from DATO is rotationally hot (50 K) and vibrationally cold (only the (0-0) vibronic transition of NO is observed). DAATO_{3.5} and ACTO primarily differ from DATO with regard to molecular structure, by the relative position of oxygen atom attachment to the tetrazine ring. Therefore, the relative position of oxygen in tetrazine-N-oxides is proposed to play an important role in their energetic behavior. N₂O is ruled out as an intermediate precursor of the NO product observed from all three molecules. Theoretical calculations at CASMP2/CASSCF level of theory predict a ring contraction mechanism for generation of the initial NO product from these molecules. The ring contraction occurs through an (S₁/S₀)_{CI} conical intersection.

Excited Electronic State Decomposition of Nitrogen Rich Energetic Materials

Nitrogen rich energetic materials have drawn considerable attention and are expected to replace traditional energetic materials such as RDX or HMX because of

their favorable energetic and explosive properties. Environmentally friendly molecular nitrogen is also expected to be the major decomposition product of these energetic materials. Nitrogen rich energetic materials known thus far include BTATz, TAGzT, TAGDNATO, and TAGDNAT. In the present work, decomposition of BTATz is studied theoretically at the CASSCF(14,11)/STO-3G level of theory. BTATz is a tetrazine based energetic molecule and theoretical calculation suggests that a tetrazine ring opening mechanism is involved in the excited electronic state decomposition of this molecule. Decomposition of BTATz is calculated to occur through an $(S_1/S_0)_{CI}$ conical intersection and produces rotationally cold N_2 product on the ground state. Experimental justification of this theoretical prediction can be obtained through state specific detection of N_2 product using either (2+2) REMPI employing $N_2^+ \leftarrow \tilde{a}^1\Pi_g \leftarrow \tilde{X}^1\Sigma_g^+$ electronic transition (at 283 nm) or (2+1) REMPI employing $N_2^+ \leftarrow \tilde{a}''^1\Sigma_g^+ \leftarrow \tilde{X}^1\Sigma_g^+$ electronic transition (at 203 nm) of N_2 . Utilizing (2+1) REMPI scheme N_2 product generated from excited electronic state decomposition of tetrazine is observed to be rotationally cold (~ 10 -15 K).

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CHAPTER 2

Experimental and Theoretical Exploration of the Initial Steps in the Decomposition of a Model Nitramine Energetic Material: Dimethylnitramine

Work presented in this chapter is published in “Bhattacharya, A.; Guo, Y. Q.; Bernstein, E. R. *J. Phys. Chem. A* **2009**, *113*, 811.” Yuanqing and I worked together on the experiments and I worked independently on the theoretical calculations.

2.1 Introduction

Elucidation of the initial steps in the decomposition of nitramine energetic materials such as RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine) and CL-20 (2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane) from both ground¹ and excited electronic states²⁻⁵ is of special relevance and importance for practical application, fundamental understanding, and improvement and development of these materials. Since even the initial step of the decomposition of these materials is an extremely rapid⁶ and exothermic reaction, it is full of challenge for physical chemist to experimentally determine the mechanisms and dynamics of the dominant decomposition reaction of nitramine energetic materials.⁷ Because of these difficulties,

dimethylnitramine (DMNA), $(\text{CH}_3)_2\text{NNO}_2$ has been studied extensively as a nitramine model system over the past decades. This simple molecule has both structural and electronic properties that are similar to large, more complex nitramine energetic materials and is more amenable to detailed experimental and theoretical studies than are the actual energetic species.

To date, initial decomposition of DMNA has been studied by thermal pyrolysis,⁸⁻¹⁰ infrared multiphoton decomposition (IRMPD),¹¹ UV-photodissociation experiments,¹²⁻¹⁵ and quantum mechanical computations.¹⁶ Nonetheless, its decomposition has not proven easy to unravel in determining the dominant reaction pathway, which is still an unresolved problem.

This chapter presents a sensible comparison of widely varied and often confusing experimental and theoretical results on DMNA decomposition. In this effort, to the best of our ability, first, all references that are related to DMNA decomposition are included in order to provide a complete and comprehensive review. Second, our experimental and theoretical results are presented and discussed. Third, all the results are compared and contrasted to reach a general conclusion on the ground and excited electronic state decomposition mechanisms for DMNA.

Our present experimental work focuses on the excited electronic state decomposition of DMNA. We have adopted a photofragmentation/fragment-detection (PF/FD) technique, for which the parent molecule is electronically excited using different UV excitation wavelengths (226 nm and 193 nm), and subsequently products are detected and their rotational and vibrational distributions are analyzed using either the same laser or a different time delayed laser. Results reported in the literature, for the

most part, support NO_2 elimination as the major decomposition channel of DMNA from excited electronic states. In contrast, our experimental observations suggest that the nitro-nitrite isomerization mechanism is favorable for excited electronic state decomposition of DMNA. We attribute the possible reason of this discrepancy to different experimental conditions, as is discussed in more detail in the General Conclusions section. Another minor decomposition channel for DMNA from excited electronic states is found to be HONO elimination. The approximate branching ratio between nitro-nitrite isomerization and HONO elimination is estimated to be 1:0.04.

Our present theoretical work focuses on both ground and electronic excited state decomposition of DMNA using a complete active space self-consistent field (CASSCF) level of theory. Present computation corroborates the fact that NO_2 elimination is the dominant pathway of thermal (ground electronic state) decomposition of DMNA; however, nitro-nitrite isomerization is the dominant pathway of excited electronic state decomposition of DMNA. Nitro-nitrite isomerization of DMNA takes place through a loose TS geometry near a conical intersection between upper and lower electronic states. Presence of such a conical intersection between upper and lower electronic surfaces along the nitro-nitrite isomerization reaction coordinate provides a direct, nonadiabatic dissociation pathway through isomerization, when DMNA evolves from the excited electronic state.

2.2 Background

Experimental: Stewart et al.⁸ performed SF_6 -sensitized laser pyrolysis of gaseous DMNA at 900 K under collisional conditions. Their observation is consistent with two

decomposition pathways: NO_2 elimination and nitro-nitrite isomerization ($((\text{CH}_3)_2\text{NNO}_2 \rightarrow (\text{CH}_3)_2\text{NONO})$) followed by dissociation of the extremely weak O-NO bond.

Lazarou and Papagiannakopoulos¹¹ performed IRMPD of DMNA in a pyrex cell within an effective temperature range of 1060-1250 K, and subsequently detected the final products using a mass spectrometer. They concluded that NO_2 elimination is the dominant decomposition channel, and no evidence corroborated either the nitro-nitrite isomerization or HONO elimination channel. Their experimental results are in agreement with the molecular beam IRMPD study of Wodke and Lee (unpublished results quoted in ref. 2), however, are in apparent disagreement with laser pyrolysis experimental results.⁸ They suggest that the apparent disagreement between their IRMPD¹¹ and laser pyrolysis experimental results⁸ is caused by temperature differences that lead to the different vibrational excitations above the N- NO_2 bond dissociation energy. Moreover, if the NO_2 elimination channel is in competition with nitro-nitrite isomerization channel in the ground electronic state, the entropy factor can make the NO_2 elimination at high temperature even more favorable than the nitro-nitrite isomerization. Extrapolating such a consideration, one would then expect a higher branching ratio between a nitro-nitrite isomerization channel and an NO_2 elimination channel at low temperature.

On the contrary, both Lloyd et al.⁹ and Fluornoy¹⁰ come to the conclusion that only NO_2 elimination occurs while DMNA is pyrolyzed in a pyrex bulb over the temperature range of 438 – 525 K. Although both of them conclude that only NO_2 elimination takes place at low temperature, no immediate explanation is given for not

observing a nitro-nitrite isomerization channel, which is also expected at low temperature (compare with IRMPD work¹¹).

McQuaid et al.¹² dissociated gaseous DMNA at room temperature under almost collisionless condition using nanosecond laser pulses (15 ns FWHM) at 248 nm photoexcitation and observed NO₂ elimination as the major decomposition channel with some evidence of minor channels such as HONO elimination, and nitro-nitrite isomerization. The branching ratio between ground state X²A₁ NO₂ formation and nitro-nitrite isomerization was estimated to be 1.5:0.001.

Stephenson and coworkers¹³ dissociated gas phase DMNA at room temperature under almost collisionless condition using picosecond laser pulses (30 ps FWHM) at 266 nm, and subsequently detected NO₂ by LIF spectroscopy using 532 nm. They observed both ground state and electronically excited NO₂ products with a larger quantum yield of the ground state X²A₁ NO₂ product. Their time resolved experiment reveals that monophotonic photodissociation of DMNA at 266 nm occurs within 6 ps.

Sausa and coworkers¹⁴ dissociated DMNA in a molecular beam using both 226 nm and 193 nm laser radiation and subsequently detected an NO product in TOFMS. They observed only NO product from decomposition of DMNA at both 226 nm and 193 nm photoexcitations. Nonetheless, they conclude that NO₂ elimination is the major decomposition channel of DMNA at these two excitation wavelengths because previous experimental results¹² corroborated the same mechanism as the major decomposition channel of DMNA at 248 nm¹² and 266 nm¹³ photoexcitations.

On the contrary, in our previous study,¹⁵ we conclude that DMNA decomposition at 226 nm photoexcitation takes place through a nitro-nitrite

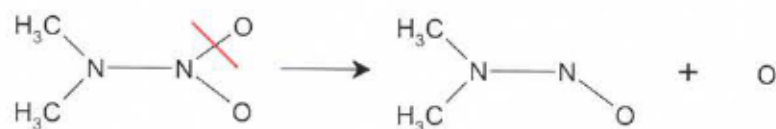
isomerization mechanism by contrasting the rotational and vibrational distributions of the product NO from photodecomposition of DMNA and that from NO₂ gas at 226 nm.

Therefore, the available experimental results on DMNA decomposition on either the ground state or the excited electronic state indicate that a number of unresolved issues clearly exist between the nitro-nitrite isomerization and NO₂ elimination mechanisms for the initial steps in the decomposition of DMNA. For a sensible comparison of these well dispersed and often confusing results on DMNA decomposition, all the various experimental conditions also need to be kept in mind. For a brief review, different plausible decomposition channels of DMNA are presented in Scheme 2.1:

Scheme 2.1

- *Elimination of O:*

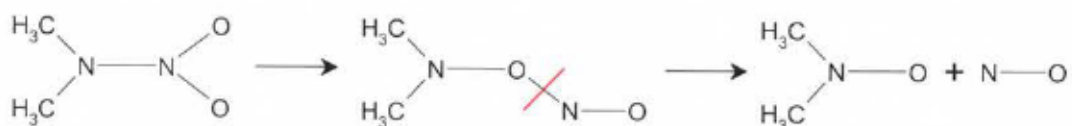
Major channel, solid DMNA at room temperature, photolysis at 253.7 nm.



- *Nitro-nitrite isomerization:*

Minor (40%) channel, room temperature gaseous DMNA, thermolysis at 900 K.

Major (96%) channel, molecular beam, photolysis at 226 and 193 nm.



- *NO₂ elimination:*

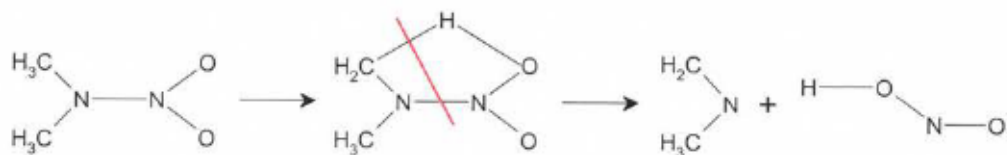
Major channel, room temperature gaseous DMNA, thermolysis at 900 K, 1060-1250 K, 466-525 K.

Major channel, room temperature gaseous DMNA, photolysis at 266 and 248 nm.



- *HONO elimination:*

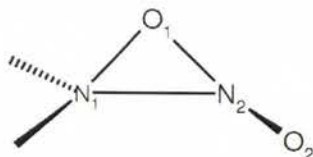
Minor (3%) channel, room temperature gaseous DMNA, photolysis at 248 nm.
 Minor (4%) channel, molecular beam, photolysis at 226 nm.



Theoretical: To date, ground state DMNA decomposition has been studied theoretically mostly by Thompson and coworkers.¹⁶ To the best of our knowledge, excited electronic state decomposition of DMNA has yet not been studied theoretically. In order to explain experimental results for both ground state and excited electronic state decomposition of DMNA, often computational work has been focused on the structurally related compound, nitramide (H_2NNO_2), because of its reduced number of heavy atoms and simplicity for computation.¹⁷⁻²⁰

The major discrepancies found among different experimental results on the DMNA decomposition are primarily concerned with two mechanisms: NO_2 elimination and nitro-nitrite isomerization. Therefore, all the theoretical results concerning these two channels are summarized below either for H_2NNO_2 or DMNA depending on the availability of the results in the literature. The nitro-nitrite isomerization activation barrier with the important geometrical parameters for the transition state and the N-NO_2 bond dissociation energy predicted for H_2NNO_2 and DMNA are summarized in Table 2.1.

Table 2.1: Optimized geometries (bond lengths in angstroms) for the transition state of the nitro-nitrite isomerization of NH_2NO_2 / $(\text{CH}_3)_2\text{NNO}_2$ / CH_3NHNO_2 in the ground electronic state.



Compounds	Nature of TS	Level of Theory	Bond Lengths	Activation Barrier (kcal/mol) ^a	Ref.
H_2NNO_2	Loose	DFT-GGA/DZVPP	N1-N2 = 2.831 N1O1 = 3.193	48.7 (48.4)	18
	Loose	MCSCF/4-31G	N1-N2 = 2.845 N1O1 = 3.214	40.7 (40.55)	17
	Tight	MP2/6-311G(d,p) QCISD(T)/6-311G(d,p)	N1N2 = 2.428 N1O1 = 1.319 N1N2 = 2.368 N1O1 = 1.119	29.7 (44.7)	19
	Loose	CASPT2(14,11)/ANO-L	N1N2 = 2.64 N1O1 = 2.00	63.55 (53.69)	20
$\text{CH}_3(\text{H})\text{NNO}_2$	Loose	B3LYP/6-311+G(d)	N1N2 = 2.618 N1O1 = 2.644	51.84 (44.64)	21
$(\text{CH}_3)_2\text{NNO}_2$	Loose	B3LYP/6-311G(d,p)	N1O1 = 2.708 N1O2 = 2.408	52.6 (39.9)	16(a)
	Tight	MP2/6-31G(d)	N1N2 = 1.90 N1O1 = 2.00	94.0 (40.0)	present result
	Loose	MP2/6-31G(d)	N1N2 = 2.80 N1O1 = 2.30	69.0	
	Loose	CASSCF(10,7)/6-31G(d)		57.0 (30.0)	

^a numbers within brackets give the calculated N-NO₂ bond dissociation energies (kcal/mol).

Saxon et al.¹⁷ and Seminario et al.¹⁸ investigated ground state nitro-nitrite isomerization and NO₂ elimination channels of H_2NNO_2 at the MRCISD/6-31G(d)/MCSCF/4-31G and nonlocal density functional theories, respectively. Both of them conclude that the nitro-nitrite isomerization and the NO₂ elimination channels would be competitive in the ground electronic state of H_2NNO_2 . As shown in the Table 2.1, the transition states (TS) reported by both Saxon et al.¹⁷ and Seminario et al.¹⁸ have loose geometries with long N1-N2 (~ 2.8 Å) and N1-O1 (~ 3.2 Å) distances.

Soto et al.^{20(a)} also investigate the nitro-nitrite isomerization and N-NO₂ bond dissociation channels for H₂NNO₂ at the CASPT2(14,11)/ANO-L level of theory and obtain a loose nitro-nitrite isomerization TS geometry: the N1O1 bond distance is 2.64 Å and the N1O2 bond distance is 2.0 Å. Employing B3LYP/6-311G(d,p) level of theory Thompson and coworkers^{16(a)} also conclude that the nitro-nitrite isomerization of DMNA occurs through a loose TS geometry and NO₂ elimination is predicted to be the main decomposition channel of gas phase DMNA in the ground state.

Morokuma and coworkers,¹⁹ in contrast, find only a tight TS geometry in the ground state of H₂NNO₂ at the MP2/6-311G(d,p) and QCISD(T)/6-311G(d,p) levels of theory: the N1-N2 distance is ~ 2.43 Å and N1-O1 is only ~ 1.32 Å. The activation energy at QCISD(T)/6-311G(d,p) level is calculated to be 29.7 kcal/mol, significantly lower than the barrier height predicted by Saxon et al.¹⁷ and Seminario et al.¹⁸ Accordingly, they conclude that a loose nitro-nitrite isomerization TS does not exist in the ground electronic state for H₂NNO₂. They also conclude that the nitro-nitrite isomerization would prevail over the NO₂ elimination at least at lower temperature because at the G2 level of theory the nitro-nitrite isomerization TS activation energy barrier is predicted to be 20.8 kcal/mol below the N-NO₂ bond dissociation energy. Note that this explanation is in contrast with the experimental observation of DMNA decomposition at low temperature.^{9,10}

With regard to investigation of excited electronic state decomposition of nitramine, Soto and coworkers^{20(b)} use the CASPT2(14,11)/ANO-L level of theory and find that the N-NO₂ bond dissociation energy for H₂NNO₂ on its S₁, S₂ and S₃ surfaces are 21.4, 5.1, and 6.2 kcal/mol, respectively. From computed potential energy curves

leading to adiabatic NO₂ elimination for H₂NNO₂ in the excited electronic states, they conclude that if NO₂ elimination takes place in the excited electronic state decomposition, NO₂ can only be generated in its ground X²A₁ or excited A1²B₂ electronic state. This result is in good agreement with the experimental results obtained by Sausa and coworkers¹² and Stephenson and coworkers.¹³ In their computation, Soto et al.,^{20(b)} however, did not focus on whether a nitro-nitrite isomerization channel is accessible in the upper excited electronic states for this compound.

Thus, the available theoretical results on decomposition of DMNA or related compounds in either the ground or excited electronic states indicate that some disagreements exist concerning the activation energy barrier and the nature of the TS associated with the nitro-nitrite isomerization. To resolve these issues, further computation on DMNA decomposition is needed at a suitable level of theory that can provide a balanced treatment of the various dissociation channels at different excitation wavelengths and within different excited states for this system.

2.3 Experimental Procedures

The experimental setup consists of ns laser systems, a supersonic jet expansion pulsed nozzle, and two vacuum chambers: a time of flight mass spectrometer (TOFMS) chamber and an LIF (laser induced fluorescence) chamber, described in detail elsewhere.²² For the ns laser experiments, a single pump/probe laser beam at 226 nm is used both to initiate dissociation of DMNA and detect the NO product following a one color (1+1) resonance enhanced two photon ionization (R2PI) scheme [$A^2\Sigma(v'=0) \leftarrow X^2\Pi(v''=0)$ and $I \leftarrow A$ transitions] through TOFMS. The UV laser wavelengths used in the ns laser experiments are generated by a pulsed dye laser, pumped by the second

harmonic (532 nm) of a Nd:YAG laser's fundamental output (1.064 μm), in conjunction with a nonlinear wavelength extension system. Typical pulse energy of the UV laser is $\sim 16 - 300 \mu\text{J/pulse}$, which gives a laser beam intensity (I) $\sim 6.5 \times 10^6$ to $1.2 \times 10^8 \text{ W/cm}^2$ for an 8 ns pulse duration at a focused beam diameter of 0.2 mm. For the detection of an OH product from DMNA through LIF, a UV laser at 226 nm is used to initiate the dissociation of the parent molecules and one additional laser (308 nm) is required to excite the OH $A^2\Sigma(v'=0) \leftarrow X^2\Pi(v''=0)$ transition. Detection of the OH product from DMNA has been precalibrated by the observation of the OH radical generated by photolysis of nitric acid (HNO_3) at 193 nm inside a quartz capillary attached to the pulse nozzle.

Photolysis of DMNA is also performed inside a quartz capillary attached to the pulsed nozzle by both 193 nm and 226 nm radiation, and subsequently products are detected in time-of-flight mass spectrometer by 118 nm ionization. An ArF excimer laser is used to generate radiation at 193 nm and the ninth harmonic (118 nm) of a seeded Nd:YAG laser is generated in a 1:10 mixture of Xe/Ar at 330 Torr pressure previously discussed elsewhere.²³

Isolated gas phase DMNA molecules are generated through a supersonic jet expansion. The nozzle employed for the sample beam generation is constructed from a Jordan Co. pulsed valve. DMNA is heated to about 350 K in a glass vial outside the nozzle and brought into the molecular beam by helium carrier gas at 30 psig backing pressure.

The experiment is run at a repetition rate of 10 Hz. The timing sequence for the pulsed nozzle, and ionization laser is controlled by a time delay generator (SRS

DG535). The molecular beam is perpendicularly crossed by a UV laser beam that is focused to a spot size of about 0.2 mm at the ionization region of a time of flight mass spectrometer. A background pressure of 1×10^{-5} Torr is maintained in the vacuum chamber during the experiment. Ions are detected by a microchannel plate detector (MCP) and fluorescence is detected by a photomultiplier tube (PMT). Signals are recorded and processed on a PC using a box car averager (SRS SR 250) and an ADC card (Analog Devices RTI-800).

2.4 Theoretical Procedures

All geometry optimizations relevant to excited electronic state decomposition of DMNA are executed at the CASSCF/6-31G(d) level of theory and with the Gaussian 03 program.²⁴ In addition, geometry optimizations relevant to ground electronic state decomposition of DMNA are performed at both the MP2 and CASSCF levels of theory with both 6-31(d) and 6-311G(d,p) basis sets. No symmetry restrictions are applied during the calculations. To explore the excited state potential energy surfaces, the active space comprises 14 electrons distributed in 11 orbitals, denoted as CASSCF(14,11) (see Figure 2.1). Orbitals used in the active space are one N nonbonding $2S_N$ orbital, two NO bonding orbitals σ_{NO} , two NO antibonding orbitals σ_{NO}^* , one delocalized ONO π -bonding orbital π_{ONO} , one delocalized ONO π -antibonding orbital π_{ONO}^* , one bonding NN orbital σ_{NN} , one NN antibonding σ_{NN}^* , one π -nonbonding orbital $n\pi_O$, and one σ nonbonding $n\sigma_O$, as illustrated in Figure 2.1.

The same active space was previously used by Soto et al.²⁰ for computations for NH_2NO_2 . To avoid convergence failure problems, a reduced (10,7) active space is also used for the excited state calculations. Vertical excitation energies are calculated by

state-averaging over the ground and excited states with equal weights for each state. Critical points (minima and transition state structures) are characterized by analytical frequency calculations, and minimum energy paths are calculated using an intrinsic reaction coordinate (IRC) algorithm implemented in the Gaussian 03. As the present Gaussian code cannot perform analytical frequency calculations using more than eight orbitals in the active space,²⁴ frequency calculations and IRC calculations, which require initial force constants, are performed using a reduced active space (10,7) with the same basis set.

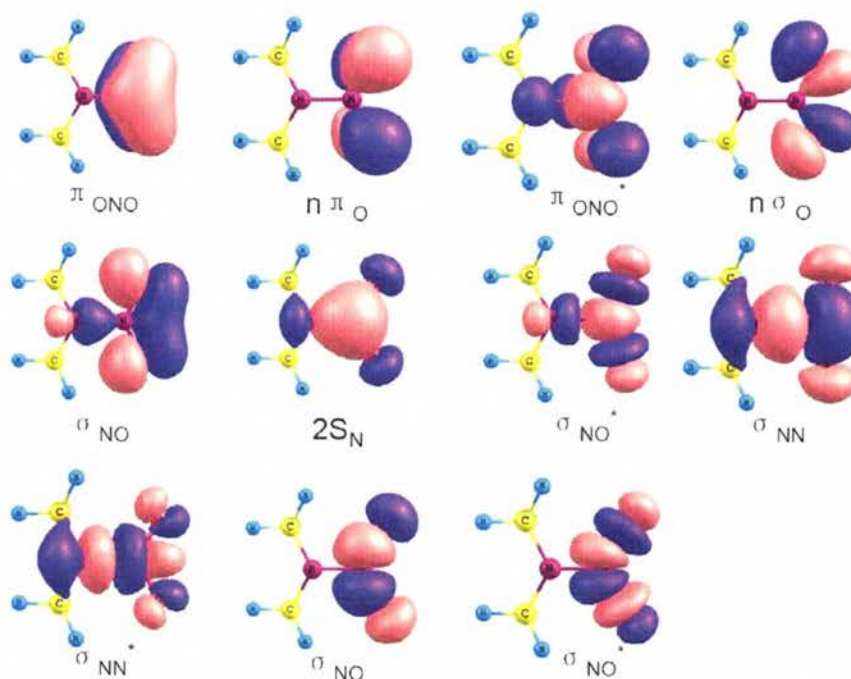


Figure 2.1: Orbitals used in the active space for CASSCF calculations for DMNA. These orbitals thus comprise the full active space (14,11) for DMNA (14 electron in 11 active orbitals).

2.5 Experimental Results and Discussion

The photofragmentation/fragment-detection (PF/FD) technique²⁵ has been employed in the investigation of the excited electronic state decomposition of DMNA.

In our PF/FD experiments, DMNA is excited to an excited electronic state by absorption of a single UV photon at different excitation wavelengths (226 nm and 193 nm), and then it decomposes into products through certain decomposition pathways. The dissociation products are subsequently detected either by the same laser or a different, time delayed laser, either in a time of flight mass spectrometer (TOFMS) or by LIF spectroscopy.

Nitric oxide (NO) is observed as a major decomposition product from the photodissociation of DMNA at 226 nm in TOFMS. This result was also previously obtained by Sausa and coworkers.¹⁴ The 226 nm excitation wavelength also corresponds to the resonance (0-0) vibronic band of the $A^2\Sigma \leftarrow X^2\Pi$ electronic transition of the NO product. Therefore, by scanning this laser excitation wavelength, a (1+1) R2PI rotationally resolved spectrum of the NO product from DMNA is obtained. Note that the DMNA absorption near the excitation wavelength is smooth, structureless, and essentially constant. In addition, a few comments can be made to clarify that the NO product is generated from the excited electronic state decomposition of DMNA following single photon absorption based on the line width of the NO mass peak. Additional kinetic energy from photofragmentation following two-photon absorption should generate additional line width for fragment mass channels. Moreover, if DMNA absorbs two photons at 226 nm sequentially, it can be fragmented into NO following ionization. This will also lead to broadening of the line width of the NO mass signal. Experimentally, the line width of the NO mass channel is observed to be about 10 ns which is the instrumental line width of our laser/TOFMS set up.

Therefore, we believe that the NO product is associated with a single photon absorption by DMNA.

Photolysis of DMNA can produce several possible primary intermediates in the initial step of photodissociation, which can finally render the NO product. These include NO₂, HONO, dimethylaminonitrite after nitro-nitrite isomerization, and dimethylnitrosamine after elimination of an O atom. Each intermediate corresponds to a different possible decomposition channel of DMNA as is illustrated in Scheme 2.1. Therefore, detection of the NO product from the photodissociation of DMNA is not an unambiguous identification of any of the four possible decomposition channels of DMNA. In order to exclude some of these possibilities, different ns laser experiments are performed, which are presented and contrasted below.

NO₂ elimination: To justify whether NO₂ is an intermediate precursor of the NO product in the excited electronic state decomposition of DMNA, investigation of the decomposition of several other nitro-containing compounds such as NO₂ gas and nitromethane is undertaken. NO₂ gas renders NO product due to photodecomposition. Nitromethane, on the other hand, is well known to produce the NO product through an NO₂ intermediate.²⁶ Therefore, comparison of the rotational and the vibrational distributions of the NO product obtained from photolysis of these nitro-containing compounds to that from photolysis of DMNA is expected to serve as a guide to determine whether NO₂ is a potential and appropriate intermediate in the excited electronic state decomposition of DMNA.

(1+1) R2PI spectra of NO from photolysis of DMNA, and other nitro-containing compounds, in the NO A²Σ (v'=0) ← X²Π (v''=0) transition region are presented and

contrasted in Figure 2.2. All the spectra are obtained under similar experimental conditions such as laser energy (50 $\mu\text{J}/\text{pulse}$), backing pressure (30 psig), collisionless molecular beam conditions, etc. The most intense band centered at 44202 cm^{-1} in these spectra is assigned to the ($Q_{11}+P_{21}$) band head²⁷ of the $A^2\Sigma^+ (v'=0) \leftarrow X^2\Pi (v''=0)$ transition of NO. Comparison of simulated spectra based on Boltzmann population distribution of the NO rotational energy levels at the $v''=0$ state to the R2PI spectra of the NO product from DMNA, NO_2 , and nitromethane generates rotational temperatures 120 K, 30K, and 600K, respectively.

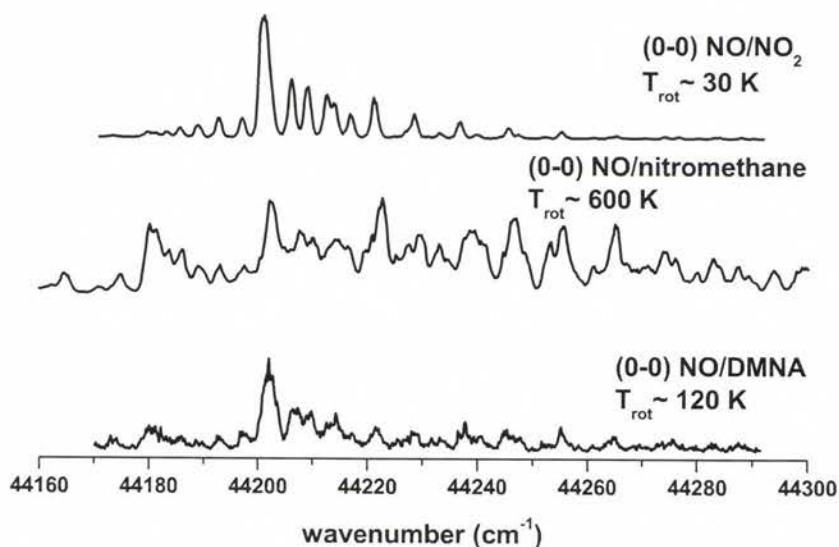


Figure 2.2: One color ($1+1$) R2PI spectra of the vibronic transitions [$A^2\Sigma^+ (v'=0) \leftarrow X^2\Pi (v''=0)$] of the NO product from the excited electronic state decomposition of DMNA and other nitro containing molecules (nitromethane and NO_2 gas). Rotational temperature simulations with Boltzmann distribution show that NO from NO_2 gas, nitromethane and DMNA generates rotational temperatures of 30, 600, and 120 K, respectively.

Photodissociation of nitromethane at 226 nm excitation renders NO product through an NO_2 intermediate.²⁶ NO from nitromethane is rotationally hotter (600 K) than that from NO_2 gas and has a vibrational distribution similar to that from NO_2 gas,

as both (0-0) and (0-1) transitions are observed. Therefore, if NO₂ is an intermediate of the excited electronic state decomposition of DMNA, the NO product from DMNA through the NO₂ precursor is also expected to have similar or hotter rotational and vibrational distributions than that of NO from NO₂ gas. If NO₂ is an intermediate in the decomposition of DMNA, the final NO product should not have rotational or vibrational distributions colder than that from NO₂ gas.

Nonetheless, on the contrary, NO from DMNA at 226 nm photoexcitation is vibrationally colder (only the (0-0) transition is observed) than that from NO₂ gas (both (0-0) and (0-1) transitions are observed), and NO from DMNA (226 nm) is rotationally hotter (120 K) than that from NO₂ gas. These differences indicate that NO₂ can not be an intermediate precursor of the NO product in the excited electronic state decomposition of DMNA. This observation is, in principle, direct evidence for the exclusion of NO₂ elimination as a major excited electronic state decomposition mechanism of DMNA. Nonetheless, one can argue that the reason for not observing the (0-1) transition of the NO product from photodecomposition of DMNA may be due to the extremely low concentration of NO₂ generated in the excited electronic state decomposition of DMNA. Therefore, to obtain an unambiguous corroboration of the fact that NO₂ is not an intermediate in the excited electronic state decomposition of DMNA, laser intensity dependence of NO spectra from DMNA and NO₂ gas is explored and contrasted below.

The (1+1) R2PI spectra of NO from photodissociation of DMNA in the NO $A^2\Sigma^+ (v'=0) \leftarrow X^2\Pi (v''=0)$ transition region for two different laser intensities are presented in Figure 2.3. Both spectra are rotationally well resolved and show similar

patterns, which produces similar rotational temperature (~ 120 K). This necessitates the conclusion that rotational temperature (in other words, R2PI spectra) of the NO product from photodissociation of DMNA at 226 nm excitation is laser intensity independent.

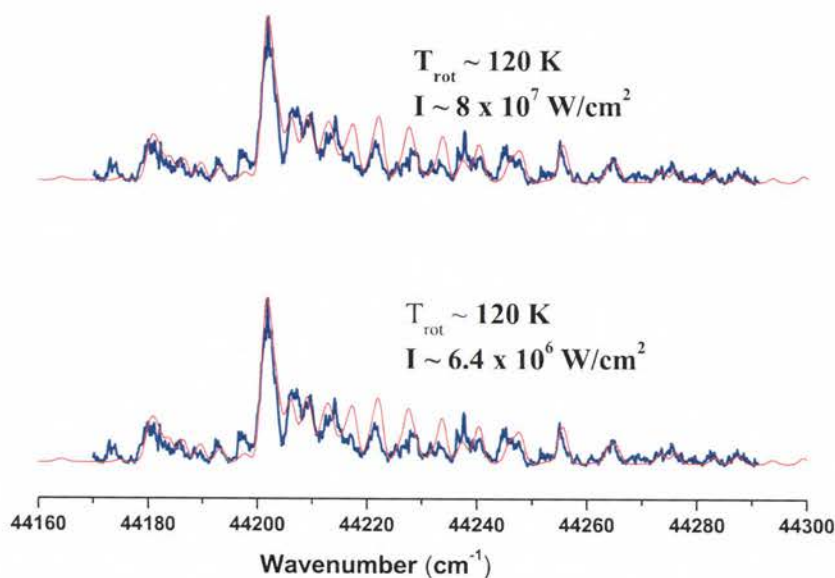


Figure 2.3: Comparison of the one color (1+1) R2PI spectra of the vibronic transitions [$A^2\Sigma^+ (v'=0) \leftarrow X^2\Pi(v''=0)$] of the NO product from excited electronic state decomposition of DMNA at different laser intensities (W/cm^2).

Similar (1+1) R2PI spectra of the NO product from photodissociation of 0.001% NO_2 seeded in He carrier gas in the same NO $A^2\Sigma^+ (v'=0) \leftarrow X^2\Pi (v''=0)$ transition region for two different laser intensities are presented in Figure 2.4. These spectra clearly show different spectral patterns at different laser intensities. At low ($6.4 \times 10^6 W/cm^2$) laser intensity, a rotational temperature of about 30 K is observed, much colder than that produced at high laser intensity ($8 \times 10^7 W/cm^2$), which is about 100 K. This behavior indicates that rotational temperature of the NO product from photodissociation of NO_2 at 226 nm excitation is laser intensity dependent.

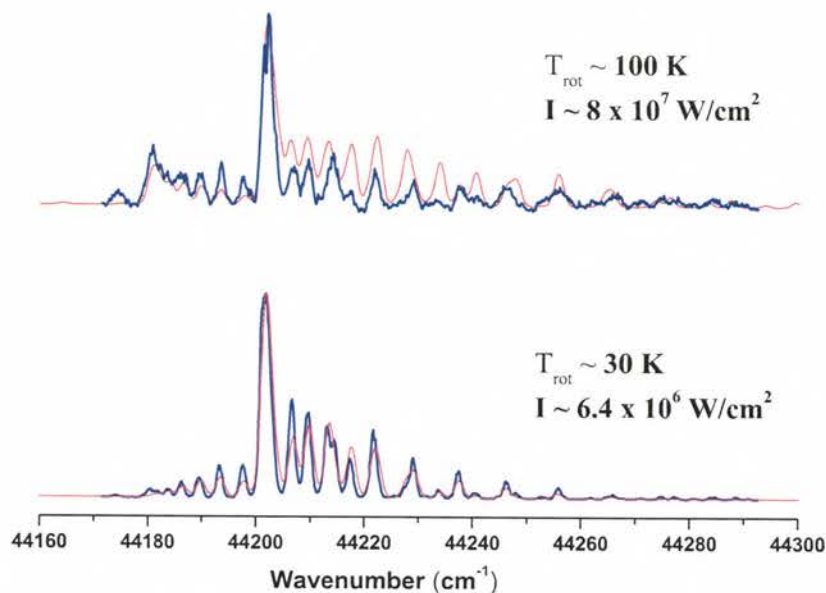


Figure 2.4: Comparison of the one color (1+1) R2PI spectra of the vibronic transitions $[A^2\Sigma^+ (v'=0) \leftarrow X^2\Pi(v''=0)]$ of the NO product from the excited electronic state decomposition of 0.001% NO_2 at different laser intensities (W/cm^2).

Photodissociation of NO_2 in this region with different laser intensities using a similar PF/FD technique was previously investigated by Im et al.^{28(a)} Although photodissociation of NO_2 near 226 nm could be studied very efficiently by probing the entire energy distribution of the fragments using the velocity map imaging technique,^{28(b)} Im et al. probed only rotational and vibrational distributions of the NO product from NO_2 using TOFMS and unambiguously determined internal temperatures by comparing the experimental REMPI spectrum of NO with the simulated one. They concluded that single photon dissociation of NO_2 through the 2^2B_2 state at 226 nm photoexcitation with low laser intensity renders a rotationally cold (~ 30 K) NO product. Multiphoton dissociation obtained at high laser intensity, on the other hand, takes place through either a Rydberg excited state or an ion-pair state producing rotationally hot (~ 100 K) NO product. If photodissociation of DMNA at 226 nm excitation renders the

primary decomposition product NO_2 in the ground state, one would expect to observe similar laser intensity dependence of the NO rotational temperature. Instead, absence of this behavior in the decomposition of DMNA at 226 nm excitation corroborates the fact that ground state NO_2 is not an intermediate in the decomposition of DMNA.

To probe the formation of excited state NO_2 photoproduct, laser induced fluorescence and emission spectroscopy are performed. If NO_2 is the primary photodecomposition product of DMNA and is generated in an excited state (either 1^2B_2 or 2^2B_1), one would expect to observe fluorescence emission from the excited state NO_2 following the photolysis of DMNA at 226 nm. The radiative lifetime for these transitions of NO_2 in the visible region is very long, typically $\sim 30 - 120 \mu\text{s}$,²⁹ indicative of a small transition oscillator strength. Radiative lifetime of NO for the transition from $\text{A}^2\Sigma^+$ state to ground state in the UV region is significantly shorter ($\sim 200 \text{ ns}$)³⁰ than that of NO_2 excited states in the visible region. Therefore, both fluorescences can easily be distinguished in LIF or emission spectroscopy. Upon photolysis of DMNA at 226 nm no emission is observed from an excited state of NO_2 . Instead, NO LIF signal with $\sim 200 \text{ ns}$ (FWHM) radiative lifetime is observed when the photolysis laser is tuned to the resonance position of the NO (0-0) transition. The LIF spectrum of NO in this region from photodissociation of DMNA, given in the Figure 2.5 (a), displays a hot rotational temperature $\sim 120 \text{ K}$.

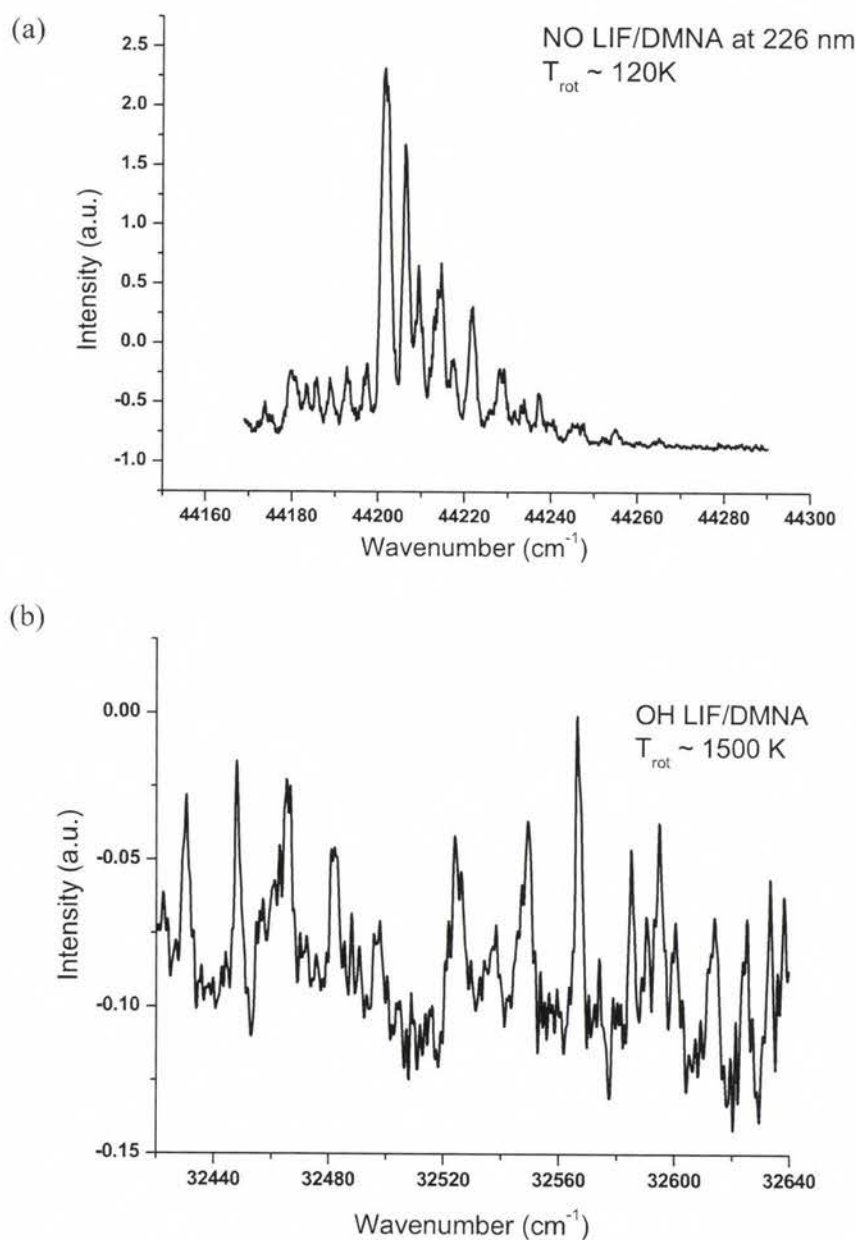


Figure 2.5: LIF spectrum of NO near 226 nm (a) and OH (b) near 308 nm from excited electronic state decomposition of DMNA at 226 nm.

Fluorescence emission with $\sim 35 \mu\text{s}$ life time from the excited state of NO_2 product following the photodissociation of nitromethane (CH_3NO_2) at 193 nm was previously observed by Butler et al. using product emission spectroscopy.³¹ By means

of translational energy distribution of products, they concluded that the primary decomposition channel of CH_3NO_2 at 193 nm renders the vibrationally hot 1^2B_2 excited electronic state of NO_2 . A similar attempt is also made by us to repeat the decomposition of nitromethane and DMNA at 193 nm. We observe fluorescence emission in the visible region with a long lifetime ($\sim 4 \mu\text{s}$) following nitromethane photodissociation (see Supplementary Information, Figure 2.S1). No emission (NO or NO_2) is observed following DMNA photodissociation at 193 nm.

Therefore, results obtained in resonance enhanced two photon ionization spectroscopy, and fluorescence emission spectroscopy for detection of the NO_2 product corroborate the fact that neither ground state (X^2A_1) nor excited state (1^2B_1 or 1^2B_2) NO_2 is a primary photodecomposition product of DMNA at 226 nm and 193 nm excitations.

HONO elimination: In order to assess whether HONO is an intermediate precursor of NO in the excited electronic state decomposition of DMNA, experimental detection of the OH radical is undertaken. If HONO is a precursor of product NO , decomposition of DMNA should produce equimolar quantities of OH and NO radicals. As OH has a high ionization energy ($\text{IE} = 13.5 \text{ eV}$), detection of OH is not performed using TOFMS. Instead, LIF spectroscopy is used to detect the OH radical from photodecomposition of DMNA. In order to detect the OH product from photolysis of DMNA by LIF spectroscopy, two lasers are required: one laser at 226 nm is used to initiate dissociation of the parent molecule and another at 308 nm is used to excite OH , corresponding to the (0-0) band of its $\text{A}^2\Sigma \leftarrow \text{X}^2\Pi$ electronic transition. Note that, DMNA does not have

any absorption at 308 nm³⁶ and therefore, 308 nm does not contribute to the dissociation process of DMNA.

The LIF spectrum of OH from photolysis of DMNA at 226 nm is shown in the Figure 2.5 (b). OH is found to have a very hot (~1500K) rotational distribution when the excitation laser (308 nm) is tuned to the resonance position of the OH (0-0) transition. Photodecomposition of DMNA at 226 nm generates less than 1.5 mV of OH LIF signal at the maximum gain of the photomultiplier tube (PMT), when OH signal intensity is fully optimized by overlapping both 226 and 308 nm beams with above absorption saturation energies. Under similar experimental conditions, the maximum LIF signal intensity of the NO product from photodissociation of DMNA at 226 nm is observed to be 50 mV when the photolysis laser is tuned to the resonance position of the NO (0-0) transition. These maximum LIF signal intensities of NO and OH can be compared to evaluate the yield ratio between these two products.

In order to estimate the yield ratio between the NO and the OH products in the excited electronic state decomposition of DMNA, however, one must relate the maximum LIF signal intensities of NO and OH to the population of the individual rotational states responsible for the transition at 120 and 1500 K, respectively. For a Boltzmann distribution for which $kT \gg 2B(J+1)$, the ratio of the population at a certain rotational J level to the entire population is given by³²

$$\frac{N_J}{N_0} = \left(\frac{hcB}{kT} \right) (2J+1) \exp \left[\frac{-BJ(J+1)hc}{kT} \right]$$

in which h is Planck's constant, c is the speed of light, k is Boltzmann's constant, and B (in cm⁻¹) is the rotational constant. This equation can determine what fraction of the entire population contributes to the maximum LIF signal intensity at a certain

temperature. Another important parameter is the Franck-Condon (FC) factor for an electronic transition, which also contributes to the maximum LIF signal intensity of a particular species.

Thus, comparing maximum LIF signal intensities of NO and OH radicals along with their respective Franck-Condon factors of the (0-0) transition and the population of rotational states responsible for the transition, the yield ratio between the NO and the OH products is calculated to be 1:0.04. The branching ratio could be determined more accurately by including the differences of the absorption line width between NO and OH species, which depend on their translational temperatures. Nonetheless, the NO absorption frequency is 44274 cm^{-1} (226 nm), which is greater than the OH absorption frequency of 32467 cm^{-1} (308 nm). Thus, the possible greater temperature to mass ratio for the OH radical can be balanced by the greater absorption frequency for the NO molecule. This implies that the absorption line width difference between NO and OH may be small. Therefore, the final influence from the absorption line width difference can be reasonably ignored because the branching ratio will not be significantly changed even if it is included in the calculation. In fact, our estimation including only rotational Boltzmann distributions and Franck Condon factor calibration shows 4% branching ratio for the HONO elimination channel which is in good agreement with that of 3% reported in previous work.¹² The large discrepancy between the OH and NO yields indicates that the HONO elimination channel has only a minor contribution to the overall excited electronic state decomposition of DMNA.

Nitro-nitrite isomerization: Experimental justification of nitro-nitrite isomerization as a potential excited electronic state decomposition pathway of DMNA is rather

complicated in nature. If nitro-nitrite isomerization takes place, one would expect to detect the $(\text{CH}_3)_2\text{NO}$ radical which is generated by nitro-nitrite isomerization followed by rapid O-NO bond scission; however, $(\text{CH}_3)_2\text{NO}$ is not observed in TOFMS employing 118 nm ionization. Two reasons for not observing $(\text{CH}_3)_2\text{NO}$ in the TOFMS can be mentioned: $(\text{CH}_3)_2\text{NO}$ neutral or cation might be unstable; and the IP of $(\text{CH}_3)_2\text{NO}$ might be above 10.5 eV. To the best of our knowledge, the IP of $(\text{CH}_3)_2\text{NO}$ is not reported in the literature. Collisions on the other hand, can stabilize the radical yielding $(\text{CH}_3)_2\text{NOH}$ (61 amu), which is a well known stable compound with low IP (9.2 eV). Therefore, in order to explore the nitro-nitrite isomerization channel, photolysis experiments at 193 nm and 226 nm are performed inside a quartz capillary attached to the pulsed nozzle.

The time of flight mass spectra, which are obtained when gaseous DMNA seeded in He carrier gas is photolysed inside a quartz capillary using 193 or 226 nm radiation with products subsequently detected by 118 nm ionization in TOFMS, are presented in Figure 2.6. The photolysis of DMNA at both 193 nm and 226 nm renders the same mass distribution of products indicating that the photodecomposition behavior of DMNA does not change at these two different excitation wavelengths.

Direct observation of 61 amu mass channel ($(\text{CH}_3)_2\text{NOH}$) in the time of flight mass spectrometer necessitates the conclusion that the rapidly produced NO arises from the nitro-nitrite isomerization mechanism, followed by extremely rapid scission of the very weak O-NO bond:



The $(\text{CH}_3)_2\text{NO}$ radical abstracts one hydrogen atom under high collisional conditions, producing the $(\text{CH}_3)_2\text{NOH}$ product. This $(\text{CH}_3)_2\text{NOH}$ mostly further decomposes to CH_2NCH_3 and H_2O products, providing a very prominent mass peak at mass channel 43 amu (CH_2NCH_3):

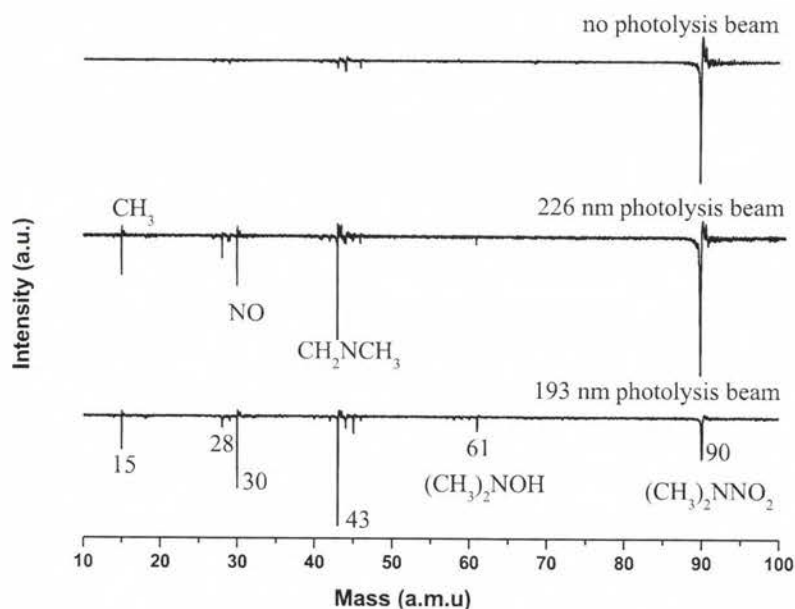


Figure 2.6: Time of flight mass spectra obtained at three different conditions: 1) photolysis of DMNA at 193 nm inside quartz capillary, subsequent product detection by 118 nm ionization (bottom), 2) photolysis of DMNA at 226 nm inside quartz capillary, subsequent product detection by 118 nm ionization (middle), 3) photolysis beam is blocked (top).

Observation of mass channel 61 amu is direct experimental evidence for the nitro-nitrite isomerization channel in the excited electronic state decomposition of DMNA; nonetheless, it does not address the inter- or intra-molecular nature of the nitro-nitrite isomerization. DMNA decomposition inside the quartz capillary happens under highly collisional conditions. At room temperature (300K), using 40 psig backing

pressure, the collision frequency is calculated to be $3.4 \times 10^{10} \text{ s}^{-1}$ for only He carrier gas inside the quartz capillary (ca. 2800 Torr pressure). This provides a mean collision time (average time between two successive collisions) of 29 ps. The laser pulse duration (8 ns) is longer than the mean collision time. Therefore, further photodecomposition of the products obtained from unimolecular decomposition of DMAN is also possible while the products are undergoing several collisions. As a result, if NO_2 elimination is the primary initial photochemical process in the unimolecular decomposition of DMNA at 193 nm and 226 nm, one would expect several collisional recombination products under these highly collisional conditions. These products could include $(\text{CH}_3)_2\text{NONO}$ (after collisional recombination of NO_2 with $(\text{CH}_3)_2\text{N}$) and $(\text{CH}_3)_2\text{NNO}$ (after collisional recombination of NO with $(\text{CH}_3)_2\text{N}$).

$(\text{CH}_3)_2\text{NNO}$ is a very stable compound with ionization energy of 9.5 eV. This is expected to be detected by 118 nm ionization; however, no signal at 74 amu ($(\text{CH}_3)_2\text{NNO}$) is observed. Instead, the only collisional product observed is $(\text{CH}_3)_2\text{NOH}$. In addition, we have already established the fact that neither ground state NO_2 nor excited state NO_2 is an excited electronic state decomposition product of DMNA. This result excludes the possibility of the intermolecular nature of nitro-nitrite isomerization by collisional recombination of NO_2 after initial NO_2 elimination; rather, a nitro-nitrite isomerization takes place through an intramolecular isomerization pathway.

Therefore, the above experimental results on the excited electronic state decomposition of DMNA necessitate the conclusion that a nitro-nitrite isomerization is the primary decomposition channel of DMNA from excited electronic states with a

minor contribution from an HONO elimination mechanism. The approximate branching ratio between nitro-nitrite isomerization and HONO elimination channels is estimated to be 1:0.04. NO_2 elimination is not the excited electronic state decomposition mechanism of DMNA. Although similar nitro-nitrite isomerization mechanism have been reported for the ground state decomposition of nitroalkanes and nitroaromatics, and even for DMNA, present experimental results are not consistent with the previous experimental reports¹²⁻¹⁴ which suggest that excited electronic state decomposition of DMNA proceeds mostly through NO_2 elimination.

Both previous experiments on the photodecomposition of gaseous DMNA at 266 nm¹³ and 248 nm¹² are done in a cell at room temperature under almost collisionless conditions. Our experiments are done under molecular beam conditions. We used 236 nm and 248 nm photolysis to photodissociate DMNA in the molecular beam; however, we did not observe any product. Therefore, experimentally we do not have an obvious immediate rationalization that can address the unresolved issues of NO_2 elimination and nitro-nitrite isomerization mechanisms in the excited electronic state decomposition of DMNA. In order to make some comment and bring these different experimental results, obtained under somewhat different experimental conditions (e.g. temperature, pressure, etc.) into harmony, detailed theoretical computation is pursued to explore the nitro-nitrite isomerization and NO_2 elimination channels for DMNA decomposition. We point out in the General Conclusions section below, combining both experimental and theoretical results, that the apparent disagreements between experimental results on DMNA decomposition arise due to different experimental conditions, in particular temperature in this instance.

2.6 Theoretical Results and Discussion

The major discrepancies found among different experimental results on both thermal and excited electronic state decomposition of DMNA are primarily concerned with two mechanisms: NO_2 elimination and nitro-nitrite isomerization. Therefore, we consider below the theoretical exploration of these two channels in order to judge which of them is energetically more favorable. We shall start with ground state calculations on DMNA decomposition because, they not only improve understanding of excited electronic state decomposition behavior of DMNA but they also justify the level of theory by establishing agreement between experimental and theoretical results. Moreover, we shall see shortly that due to presence of a conical intersection, ground and excited electronic state decomposition pathways are highly correlated along the nitro-nitrite isomerization reaction coordinate. These results and understandings are necessary and essential for providing new insight into the overall decomposition mechanism and dynamics of DMNA.

Ground electronic state decomposition: The nitro-nitrite isomerization followed by extremely weak NO-NO bond scission is a thermochemically allowed decomposition mechanism of DMNA in the ground electronic state. The nature of the transition state (TS) associated with the nitro-nitrite isomerization channel is a subject of more discussion. Both tight and loose TS geometries are reported in the literature for the nitro-nitrite isomerization in the ground state (see Table 2.1). A tight TS geometry corresponds to an isomerization for which rotation of NO_2 is substantial at short N-N bond length. A loose TS geometry, on the other hand, corresponds to an isomerization for which rotation of NO_2 does not happen until the N-N bond is elongated

substantially. The nitro-nitrite isomerization activation barriers, along with important geometrical parameters and N-NO₂ bond dissociation energies estimated by different groups for DMNA and H₂NNO₂, are summarized in the Table 2.1. Note that localization of both tight and loose transition states for either DMNA or NH₂NO₂ at the same level of theory has not been possible.

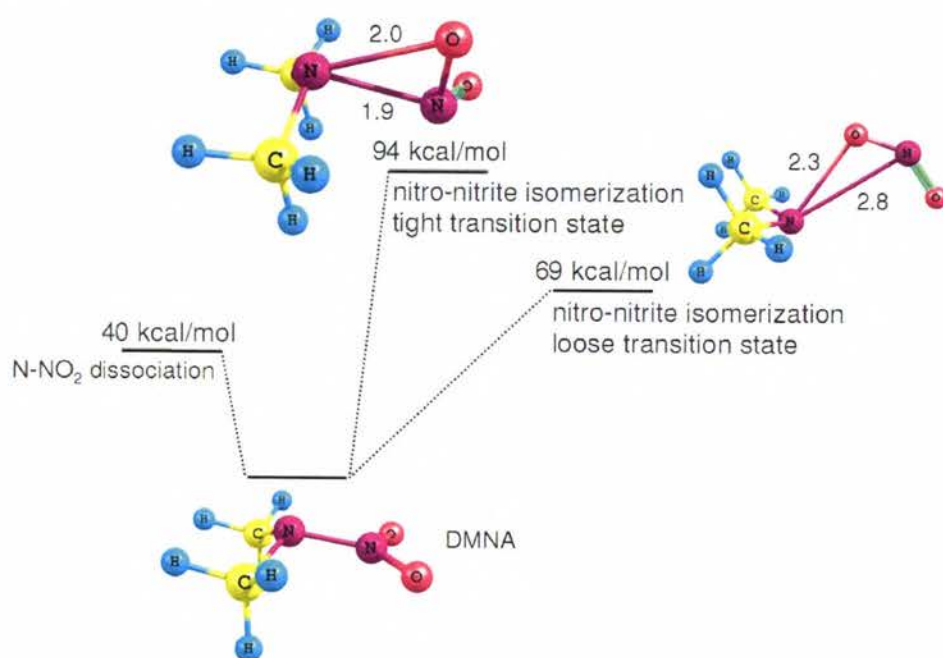


Figure 2.7: Both tight and loose transition state geometries for the DMNA nitro-nitrite isomerization optimized at the MP2/6-31G(d) level of theory for the ground electronic state. Relative activation energies are given and can be compared to the N-NO₂ bond dissociation energy computed at the same level of theory.

In contrast, we are able to localize both tight (with a short N-N bond distance) and loose (with a long N-N bond distance) TSs on the ground electronic state surface of DMNA at the MP2/6-31G(d) level of theory, as shown in Figure 2.7. In the tight transition state, the N1N2 bond distance is predicted to be 1.9 Å, and N1O1 is predicted to be 2.0 Å (see Figure 2.7). The activation energy at the MP2/6-31G(d) level is

calculated to be 94 kcal/mol. In the loose transition state geometry, the N1N2 bond distance is predicted to be 2.8 Å, and N1O1 bond distance is predicted to be 2.3 Å (see Figure 2.7). The activation energy barrier of the loose TS is calculated to be 69 kcal/mol, significantly lower in energy than that of tight TS at the MP2/6-31G(d) level.

In spite of an exhaustive search to reproduce both tight and loose TS geometries for the ground electronic state at the CASSCF(10,7)/6-31G(d) level of theory, however, only a loose TS geometry for the nitro-nitrite isomerization of DMNA is obtained. In addition, in the neighborhood of the nitro-nitrite tight TS region predicted at the MP2 level, an $(S_1/S_0)_{CI}$ conical intersection is localized at both CASSCF(10,7) and CASSCF(14,11) levels of theory with the 6-31G(d) basis set. The adiabatic energy gap between the S_0 and the S_1 surfaces near the $(S_1/S_0)_{CI}$ conical intersection is computed to be 11 cm^{-1} at the CASSCF(10,7)/6-31G(d) level.

Similar behavior was also found by Soto et al.^{20(a)} for the ground state potential energy surface of structurally related NH_2NO_2 at both CASSCF and CASPT2 levels of theory with an ANO-L basis set. They found that CASSCF and CASPT2 levels of theory could not localize any tight nitro-nitrite TS, but could localize a loose nitro-nitrite TS. In addition, near the tight TS region predicted at the MP2 level, they could localize an $(S_1/S_0)_{CI}$ conical intersection. They attributed this discrepancy between multiconfigurational (e.g., CASSCF calculation) and monoconfigurational (e.g., HF calculations) methods to the presence of $(S_1/S_0)_{CI}$ conical intersection and concluded that the presence of this conical intersection in the region of the nitro-nitrite isomerization TS repels the S_0 surface down, destroying the tight TS for the nitro-nitrite isomerization.

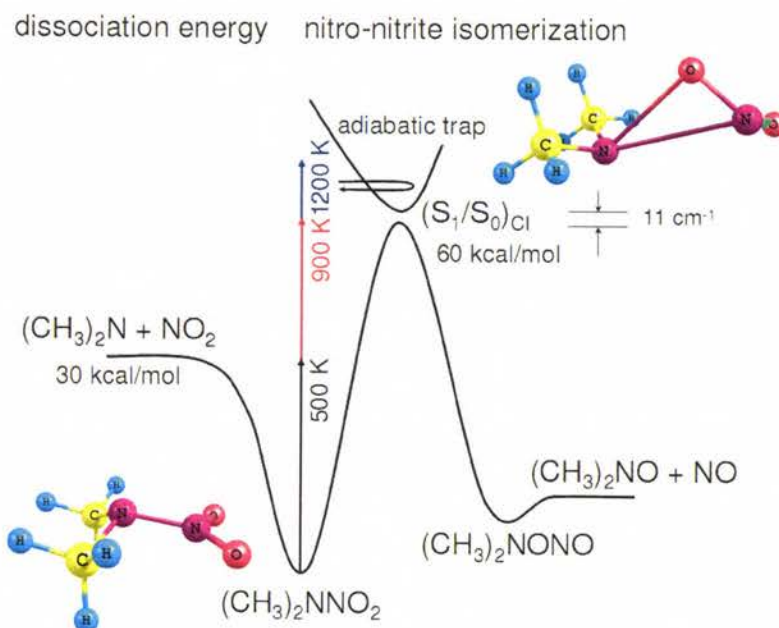


Figure 2.8. A schematic diagram of the N-NO₂ bond dissociation and nitro-nitrite isomerization pathways presented along two different directions with their respective energies of dissociation and activation computed at CASSCF(10,7)/6-31G(d) level of theory. Nitro-nitrite isomerization TS exists near the (S₁/S₀)_{CI} conical intersection and its energy is calculated to be of ~3 kcal/mol below the energy barrier of the conical intersection. The adiabatic energy gap between the S₁ and S₀ surfaces near (S₁/S₀)_{CI} is calculated to be 11 cm⁻¹.

In accord with Soto et al., we also believe that nitro-nitrite isomerization of DMNA takes place through a loose geometry which is predicted at CASSCF(10,7)/6-31G(d) level of theory. In addition, we also believe that the monoconfigurational methods (such as MP2) may overestimate the energy barrier of the tight nitro-nitrite isomerization TS because they cannot judge how the S₀ surface topology can be affected by the proximity of the S₁ surface near the (S₁/S₀)_{CI} conical intersection. Therefore, only the CASSCF level of theory (or MRCI, CASPT2 approaches) will provide the most reasonable theoretical picture of the decomposition of DMNA.

A schematic diagram for the N-NO₂ bond dissociation energy and nitro-nitrite isomerization activation barrier with (S₁/S₀)_{CI} conical intersection of DMNA computed at CASSCF(10,7)/6-31G(d) level is illustrated in the Figure 2.8. The N-NO₂ bond dissociation energy and the nitro-nitrite isomerization activation barrier are predicted to be 30 and 57 kcal/mol, respectively. The energy barrier for (S₁/S₀)_{CI} conical intersection is predicted to be 60 kcal/mol. Our present computation at the CASSCF(10,7)/6-31G(d) level of theory on the decomposition of DMNA on the ground electronic surface not only predicts the true nature of the TS for nitro-nitrite isomerization, but can also explain and integrate all the experimental results for the thermal decomposition of DMNA, as presented in the next three paragraphs.

(a) At relatively low temperature (e.g., ~500 K) thermolysis, when the system barely reaches the N-NO₂ bond dissociation energy (30 kcal/mol), NO₂ elimination is expected to be the only decomposition mechanism for DMNA. Due to low vibrational energy excitation ((3N-6)RT ~ 29 kcal/mol) at that temperature, DMNA cannot surmount the activation barrier for the nitro-nitrite isomerization. This has been observed by Lloyd and Fluornoy in their pyrolysis experiment of gaseous DMNA,^{9,10} which renders NO₂ elimination as the only decomposition channel for DMNA near 500 K.

(b) At higher temperature (e.g., ~ 900 K), when the system can also surmount the activation barrier (57 kcal/mol) of the nitro-nitrite isomerization, both NO₂ elimination and nitro-nitrite isomerization channels are expected to play a role in the overall decomposition mechanism and dynamics for DMNA. The branching ratio between these two channels will depend on many factors, e.g., enthalpy and entropy of the

reaction, electronically nonadiabatic transitions, etc. Electronic nonadiabatic effects are indeed important if the coupling between the two interacting adiabatic electronic states is weak enough and the adiabatic energy gap between two electronic states is not large enough near the respective conical intersection. The probability of a nonadiabatic surface jump near a conical intersection depends on the energy gap between the two adiabatic surfaces near that point.³³ If the energy gap (the magnitude of the coupling) between two adiabatic surfaces near the conical intersection point is small enough (weak coupling between the two surfaces), the rate of nonadiabatic transition through this point from one adiabatic surface to another adiabatic surface becomes fast. An illustration of such a consideration was first predicted by Landau and Zener³⁴ and later has been found in many organic compounds.³⁵ The adiabatic energy gap between the S_1 and S_0 surfaces near $(S_1/S_0)_{CI}$ is computed to be 11 cm^{-1} (see Figure 2.8). Therefore, the nitro-nitrite isomerization channel in the ground state can be frustrated due to the presence of the weakly coupled $(S_1/S_0)_{CI}$ conical intersection by transferring some of the ground state populations to the upper electronic surface. Therefore, at high enough temperature, when the system can surmount the nitro-nitrite isomerization activation barrier, NO_2 elimination is still expected to be the major decomposition channel. This has been observed by Golden and coworkers.⁸ They observed only 20 % of the total decomposition of DMNA goes through nitro-nitrite isomerization at 900 K.

(c) At even higher temperature (1200 K), an additional important factor, the entropy of the reaction, can also play a role in the overall decomposition mechanism and dynamics for DMNA on the ground potential energy surface. In a chemical reaction if the number of particles in the system increases, entropy of the reaction also increases. Therefore,

the NO₂ elimination reaction channel possesses a positive entropy of reaction that becomes a significant factor at higher temperature ($\Delta G = \Delta H - T\Delta S$). This can explain why, for the laser pyrolysis experiments at 900 K, the nitro-nitrite isomerization represents more than 20 % of the total decomposition of DMNA, but in the IRMPD experiment at 1150 K, this pathway is less than 10%.¹¹

Excited electronic state decomposition: With regard to the discussion of the excited electronic state decomposition of DMNA, a comparison between the computed vertical excitation energies and the experimental excitation energies has been done in order to assess which excited states are relevant to our experimental observations. The vertical excitation energies (E_{vert}) for DMNA, calculated at their CASSCF(10,7)/6-31G(d) optimized Franck-Condon (FC) geometry (ground state minimum) of C₁ symmetry are listed in Table 2.2.

Table 2.2: CASSCF(10,7)/6-31G(d) calculated vertical excitation energies and relative energies of the conical intersections with respect to the energy of FC geometry, optimized at the same level of theory.

State/CI	Configuration	ΔE (eV)
S ₁ (FC)	(n σ _O , π^*)	4.83
S ₂ (FC)	(n σ _O , π^*)	5.65
S ₃ (FC)	(n π _O , π^*)	6.6
(S ₁ /S ₀) _{CI}	-	2.6
(S ₂ /S ₁) _X ^a	-	4.8
(S ₂ /S ₁) _{CI}	-	4.2

^a Two S₂/S₁ conical intersections are localized in the S₂ surface, one at shorter N-N bond distance defined as (S₂/S₁)_X and another at longer N-N bond distance defined as (S₂/S₁)_{CI}. See text for more details.

The CASSCF calculations show that the three lowest-lying excited states for DMNA are (n, π^*), (n, π^*) and (π , π^*) states, which correspond to S₁, S₂, and S₃ excited electronic states, respectively. The calculated vertical excitation energies of the S₂

(n,π^*), and S_3 (π,π^*) states are 5.65 and 6.6 eV (see Table 2.2), respectively, which are in good agreement with the experimental values of 5.39 and 6.42 eV.³⁶ This comparison reveals that dynamical correlation (omitted in a CASSCF calculation but included in MP2 correlated CASSCF calculations) is not the major contributor to these excited electronic states. In addition, the CASSCF computation with a (10,7) active space gives a reasonable treatment of the relevant excited states. Comparing the excitation energies (5.49 eV at 226 nm, 6.4 eV at 193 nm) used in this work with the calculated vertical excitation energies (5.65 eV and 6.6 eV, Table 2.2) of the S_2 (n,π^*) and S_3 (π,π^*) excited states of DMNA, one finds that DMNA is excited to its S_2 (n,π^*) and S_3 (π,π^*) excited states by 226 nm and 193 nm excitation wavelengths, respectively. Here, we explore only S_0 , S_1 , and S_2 electronic surfaces of DMNA theoretically in order to explain our experimental results obtained at 226 nm photoexcitation; however, as photodecomposition behavior of DMNA does not change at 193 and 226 nm photoexcitations (see Experimental Results and Discussion), we anticipate similar behavior for S_3 state which is involved at 193 nm photoexcitation.

A schematic one dimensional projection of the multidimensional singlet potential energy surfaces (S_0 , S_1 , and S_2) of DMNA with locations and structures of different critical points is plotted in Figure 2.9. Path arrows in this figure indicate the classical trajectory of the possible decomposition pathway for the excited electronic state decomposition of DMNA. Potential energy curves are explicitly calculated using IRC algorithm. Computed curves are given in the Supplementary Information (Figure 2.S2-2.S5).

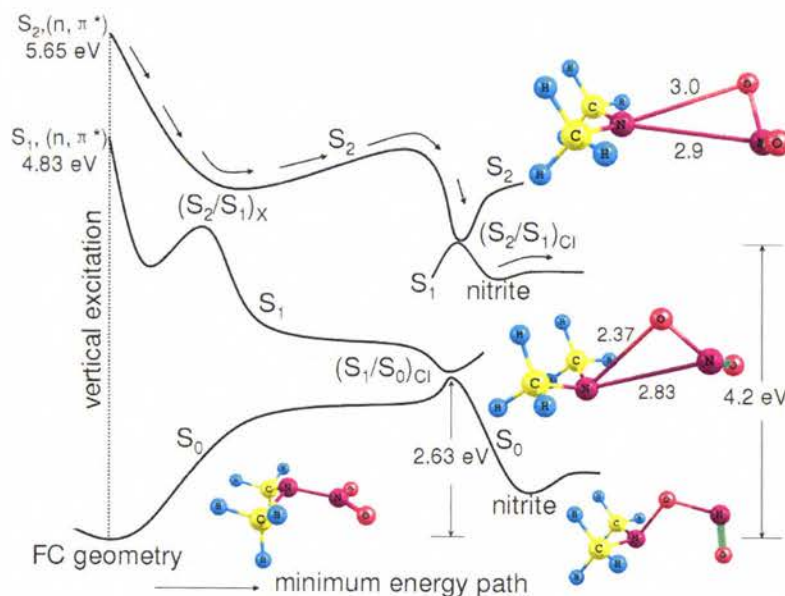


Figure 2.9: One dimensional projection of the multidimensional electronic potential energy surfaces of DMNA computed at the CASSCF(10,7)/6-31G(d) level of theory. Note that the $(S_2/S_1)_X$ conical intersection is nonadiabatically weakly coupled and the adiabatic energy gap near this conical intersection is computed to be 485 cm^{-1} . $(S_2/S_1)_{CI}$ and $(S_1/S_0)_{CI}$ are relatively nonadiabatically strongly coupled conical intersections. Path arrows represent the classical trajectory of the plausible excited electronic state decomposition mechanism of DMNA.

The optimized ground state geometry (FC geometry) of DMNA has a non-planar arrangement of the CNNO moiety (see Figure 2.9). Above the ground state surface, two stationary points are localized: (1) a transition state on the S_1 surface; and (2) a minimum on the S_2 surface. In addition, three conical intersections between singlet surfaces can be localized: (1) $(S_1/S_0)_{CI}$, conical intersection between S_1 and S_0 surfaces; (2) $(S_2/S_1)_X$, conical intersection between S_2 and S_1 surfaces at short N-N bond distance; and (3) $(S_2/S_1)_{CI}$ conical intersection between S_2 and S_1 surfaces at long N-N bond distance. The structure of DMNA at both $(S_1/S_0)_{CI}$ and $(S_2/S_1)_{CI}$ represents a loose geometry in which the NO_2 moiety interacts with the $(\text{CH}_3)_2\text{N}$ moiety from a long distance ($\sim 2.8\text{ \AA}$). The relative CASSCF energies of the conical intersections on both

excited and ground singlet potential energy surfaces of DMNA with respect to the energy of ground state FC geometry are listed in Table 2.2.

On the basis of the results presented above, we can make different plausible pictures of the dissociation mechanism and dynamics for DMNA. Comparing vertical excitation energies of different singlet excited electronic states (see Table 2.2), one can infer that irradiation of isolated molecular DMNA at 226 nm can populate the S_2 state, and at 193 nm can populate the S_3 state. As can be seen in Figure 2.9, vertical excitation to the FC point in the S_2 state can potentially lead to the nonadiabatic nitro-nitrite isomerization through $(S_2/S_1)_{CI}$ conical intersection. This conical intersection is energetically accessible from the FC point of the S_2 surface, because this point is lower in energy than the vertical excitation to the S_2 surface, and negligible energy barrier exists along this decomposition pathway. After crossing the $(S_2/S_1)_{CI}$ conical intersection, DMNA can be directed either to the isomerization product or to the NO_2 elimination product on the S_1 surface. On the S_1 surface the isomerization channel is calculated to be the minimum energy pathway (see Supplementary Information, Figure 2.S5); note that following the $(S_2/S_1)_{CI}$ on the S_1 surface, a 3 kcal/mol energy barrier exists for the NO_2 elimination pathway, but no energy barrier is found for the nitro-nitrite isomerization channel.

Another possible decomposition pathway from the FC point of the S_2 surface would be nonadiabatic deactivation of the molecule to the S_1 surface through the $(S_2/S_1)_X$ conical intersection. After crossing the $(S_2/S_1)_X$ conical intersection, DMNA additionally can be directed to another surface crossing, the $(S_1/S_0)_{CI}$ conical intersection. This will finally lead the system to the nitro-nitrite isomerization, which is

predicted to be the minimum energy pathway on the ground electronic surface. The actual pathway will depend on different factors, such as the rate of IVR and the rate of nonadiabatic transition through the different conical intersections, which can only be assessed by dynamical calculations, e.g., using multiconfiguration time-dependent Hartree (MCTDH).³⁷ Nonetheless, a few comments can be made on the most plausible mechanism of excited electronic state decomposition of DMNA.

The rate of nonadiabatic transition through a conical intersection depends on the energy gap between the two adiabatic surfaces. A small (weakly avoided crossing) energy gap enhances the probability of nonadiabatic transition from upper electronic state to the lower electronic state near the conical intersection. The computed energy gap between S_2 and S_1 adiabatic surfaces near $(S_2/S_1)_X$ and $(S_2/S_1)_{CI}$ are 487 cm^{-1} and 0.73 cm^{-1} , respectively, at the CASSCF(10,7)/6-31G(d) level of theory. Therefore, in a dynamical sense, the nonadiabatic transition through $(S_2/S_1)_{CI}$ will dominate that through $(S_2/S_1)_X$. As a result, nitro-nitrite isomerization through the $(S_2/S_1)_{CI}$ conical intersection on the S_1 surface may be expected to be the major decomposition channel of DMNA from FC point of S_2 surface.

The conclusion of our theoretical study is thus that along the nitro-nitrite isomerization reaction coordinate, the electronic potential energy surfaces ($S_{0,1,2}$) of DMNA are highly coupled, yielding various conical intersections between two electronic adiabatic surfaces. This provides a direct nonadiabatic minimum energy pathway for a nitro-nitrite isomerization when the molecule evolves from the upper electronic surface to the lower electronic surface. Therefore, if the molecule undergoes a nonadiabatic transition through $(S_2/S_1)_{CI}$, nitro-nitrite isomerization will dominate

over NO_2 elimination. This explains why our experimental results corroborate nitro-nitrite isomerization as the primary pathway for the excited electronic state decomposition of DMNA. Note, however, that for the isolated molecule conditions of our experiment, the energy in a DMNA molecule following photoexcitation remains constant until fragmentation occurs. The above results deal only with the partitioning of this energy amongst the different nuclear degrees of freedom of DMNA.

Similar electronic nonadiabatic effects, however, can hinder the adiabatic nitro-nitrite isomerization pathway on the ground state potential energy surface, as discussed above. The NO_2 elimination reaction coordinate, on the other hand, does not suffer from such an electronic nonadiabatic effect. Therefore, adiabatic NO_2 elimination is expected to dominate over adiabatic nitro-nitrite isomerization on the ground state potential energy surface. This explains why at even high temperature NO_2 elimination is a favorable pathway for thermal decomposition of DMNA.

2.7 General Conclusions

This chapter attempts to describe the current state of knowledge for the decomposition of DMNA. The main focus is on the initial unimolecular decomposition reaction of DMNA under isolated conditions. The different experimental and theoretical results, together with our results, are critically judged in order to rationalize all the experimental and theoretical findings.

Formation of NO and OH radicals has been studied experimentally following decomposition of DMNA at 226 nm and 193 nm photoexcitations. Both LIF and TOFMS techniques are used for product detection under molecular beam conditions. Contrary to the previous results on DMNA photodecomposition, neither ground state

NO_2 nor excited state NO_2 is experimentally observed to be an excited electronic state decomposition product of DMNA. Instead, nitro-nitrite isomerization followed by elimination of NO is found to be the major decomposition channel of DMNA from excited electronic states with a minor contribution from HONO elimination channel. The approximate branching ratio between nitro-nitrite isomerization and HONO elimination channels is experimentally estimated to be 1:0.04.

The NO_2 elimination and nitro-nitrite isomerization channels are also explored through theoretical calculations at the CASSCF level in order to judge which one would be energetically more favorable over the other in the overall decomposition of DMNA. Present computations show the importance of the $(\text{S}_2/\text{S}_1)_{\text{CI}}$ conical intersection in the nitro-nitrite isomerization reaction coordinate, as it provides a direct nonadiabatic decomposition pathway in the excited state through isomerization when DMNA evolves from the FC point of the S_2 state, which is experimentally accessed by 226 nm photoexcitation of DMNA. On the ground electronic surface (during thermal decomposition), however, a similar $(\text{S}_1/\text{S}_0)_{\text{CI}}$ conical intersection hinders the isomerization exit channel due to a very small adiabatic energy gap (11 cm^{-1}) between S_1 and S_0 surfaces near this conical intersection (shown in Figure 2.8). Thereby, where electronic nonadiabatic effects favor a nitro-nitrite isomerization channel for excited electronic state decomposition of DMNA, the same effect hinders this isomerization channel on the ground electronic surface. The NO_2 elimination reaction coordinate is not hindered in the ground state by such an electronic nonadiabatic effect. As a result, NO_2 elimination is favored in the ground state decomposition of DMNA. In addition, the entropy factor can also favor the NO_2 elimination channel in the thermal

decomposition of DMNA at high temperature because this decomposition channel possesses positive entropy of reaction.

Therefore, among four possible initial decomposition mechanisms of DMNA we conclude that the NO_2 elimination is the primary mechanism for thermal decomposition of DMNA. In the excited electronic state decomposition of DMNA, on the other hand, nitro-nitrite isomerization is the primary decomposition mechanism. Our results successfully corroborate and explain the ground state behavior of DMNA decomposition bringing all the experimental and theoretical results on thermal decomposition of DMNA into agreement. Nonetheless, our results are still in contrast with previous photodecomposition results on DMNA, which suggest that NO_2 elimination is the primary channel of decomposition of DMNA in the excited electronic states.

In order to bring harmony to all the photodecomposition results, the only logical rationalization we can offer is that different experimental conditions perhaps can change the photodecomposition behavior of DMNA. What is anticipated from our present computational study is that during excited electronic state decomposition of DMNA, nitro-nitrite isomerization takes place near a conical intersection through a loose geometry for which the NO_2 moiety interacts with the $(\text{CH}_3)_2\text{N}$ moiety from a considerably long distance ($\sim 2.8 \text{ \AA}$) through a relatively weak interaction ($\sim 3 \text{ kcal/mol}$). Therefore, if enough vibrational energy is provided to the intermolecular modes of these two moieties during this excited state isomerization process, they can promptly diffuse away and can undergo NO_2 elimination.

At room temperature, molecules are thermally hot (~ 300 K). Therefore, hot parent molecules can provide enough vibrational energy to the intermolecular modes of DMNA that the NO_2 and $(\text{CH}_3)_2\text{N}$ moieties can diffuse away in spite of their initial close proximity during isomerization, resulting in NO_2 elimination as the major decomposition channel. This might be the plausible reason why decomposition of DMNA, at 248 nm and 266 nm photoexcitations at room temperature under almost collisionless conditions, renders NO_2 elimination.

In the molecular beam, however, molecules are extraordinarily cold (~ 1 K) and thus the two moieties NO_2 and $(\text{CH}_3)_2\text{N}$ can remain in close proximity, rendering nitro-nitrite isomerization as the major decomposition channel. The same is possible even at room temperature in a dense gaseous medium, for which cage effects can again keep the two moieties in the close proximity, resulting in nitro-nitrite isomerization as a major decomposition channel. Both have been observed in our experiments.

Therefore, the general conclusion is that the decomposition of DMNA in excited electronic states takes place mostly through a nitro-nitrite isomerization (loose TS) reaction mechanism. The products of this excited electronic state unimolecular decomposition reaction depend on the experimental conditions, however. Nitro-nitrite isomerization in the excited electronic state happens through a loose geometry near a conical intersection between upper and lower electronic states. If the parent molecule is thermally hot and the decomposition takes place under almost collisionless conditions, the NO_2 elimination channel can be the major decomposition pathway from the excited electronic state. Under molecular beam conditions (very cold parent molecules) or in a dense gaseous medium, however, the nitro-nitrite isomerization channel can be the

major decomposition pathway from the excited electronic state. In the ground state (thermal decomposition), on the other hand, NO₂ elimination is the major decomposition channel of DMNA.

2.8 Acknowledgment

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2.9 References

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Supplementary Information

Figure 2.S1: NO_2 fluorescence emission observed following decomposition of nitromethane at 193 nm. Note that the observed $\sim 4 \mu\text{s}$ life time of the excited state NO_2 is probably due to the molecular beam longitudinal velocity ($\sim 2000 \text{ m/s}$) and the short ($< 2 \text{ cm}$) detection range for fluorescence. The actual lifetime for this NO_2 fluorescence is ca. $32 \mu\text{s}$; within this time, excited molecules escape from the fluorescence collection region. The NO fluorescence has a ca. 200 ns lifetime. See text for more discussion of these points.

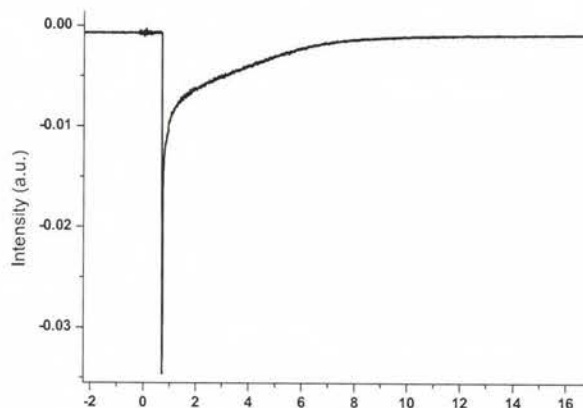


Figure 2.S2: Minimum energy pathway computed starting from the FC point on the S_2 surface of DMNA to the $(S_2/S_1)_{CI}$ conical intersection following the S_2 gradient and from $(S_2/S_1)_{CI}$ on the S_1 surface following the S_1 gradient.

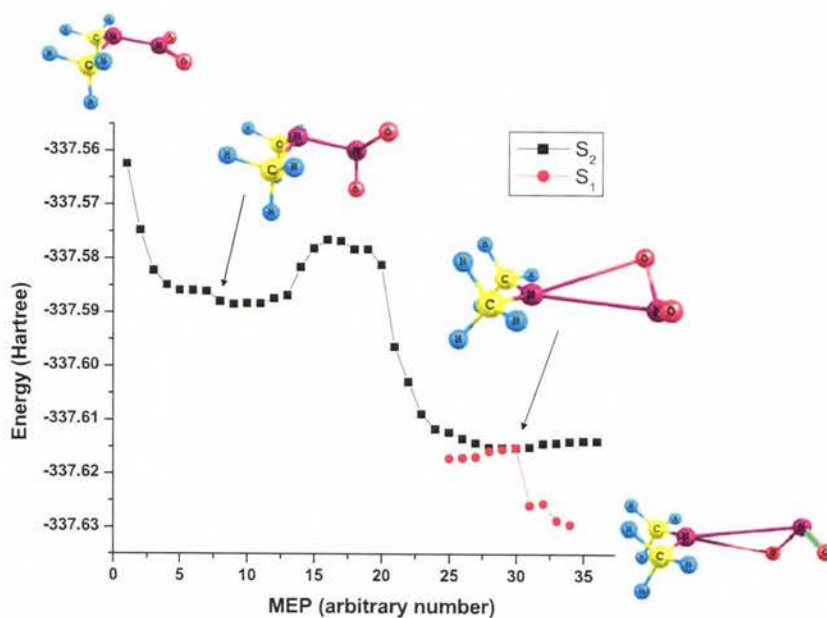


Figure 2.S3: Potential energy surface scan of DMNA along N-NO₂ bond elongation reaction coordinate at the CASSCF(14,11)/6-31G(d) level of theory.

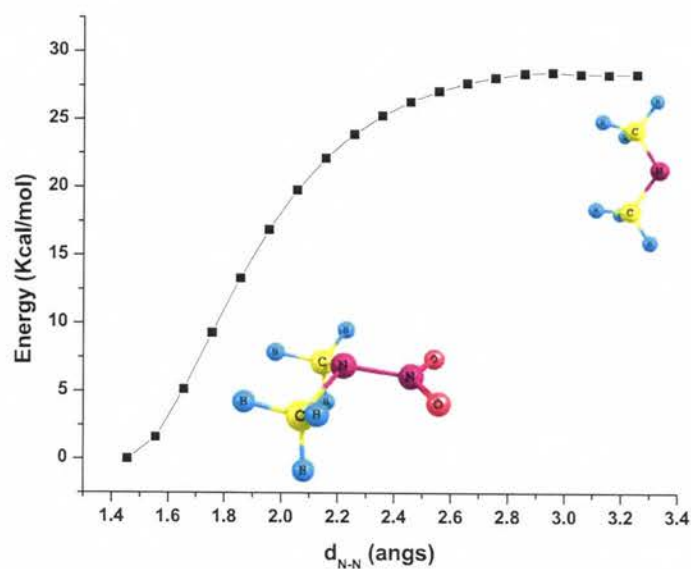


Figure 2.S4: Potential energy surface scan along the N-O bond formation reaction coordinate of nitro-nitrite isomerization channel of DMNA.

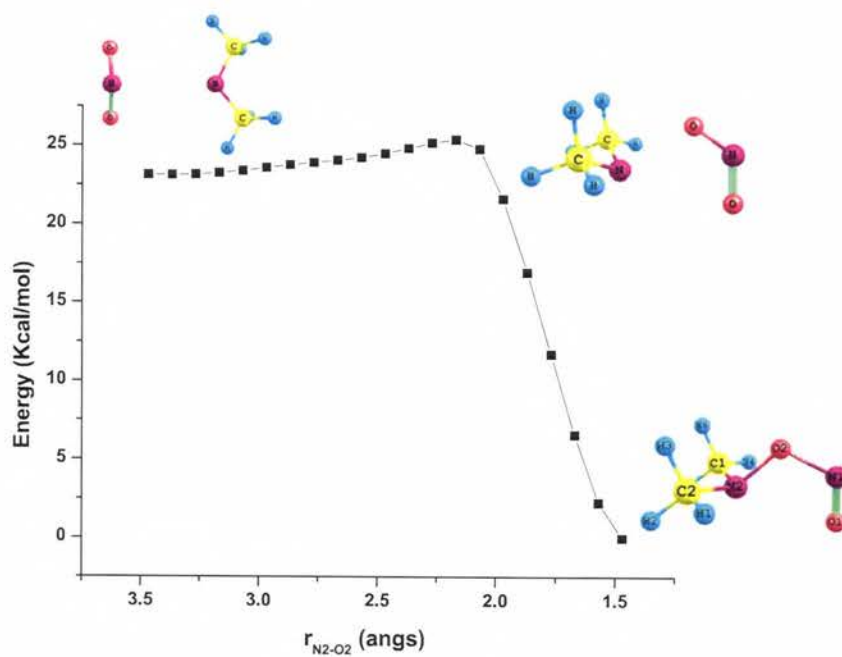
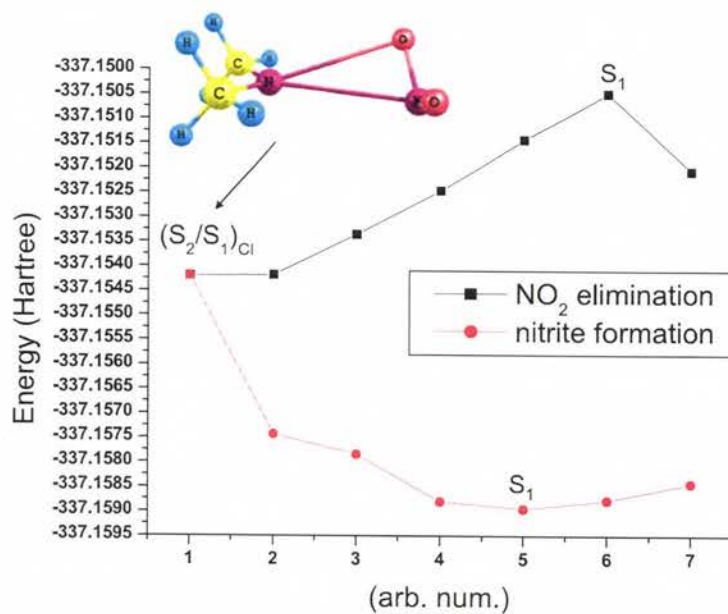


Figure 2.S5: Potential energy surface scan of DMNA along N-NO₂ bond elongation (square) and N-ONO bond formation (circle) reaction coordinates from (S₂/S₁)_{CI} conical intersection following S₁ gradient vector at CASSCF(10,7)/4-31G level of theory.



CHAPTER 3

Photodissociation Dynamics of Nitromethane at 226 and 171 nm at Both Nanosecond and Femtosecond Time Scales

Work presented in this chapter is published in “Guo, Y. Q.; Bhattacharya, A.; Bernstein, E. R. *J. Phys. Chem. A* **2009**, *113*, 85.” Yuanqing and I worked together on the experiments described below.

3.1 Introduction

As a low sensitivity nitro-containing energetic material, nitromethane is widely used in racing fuels, propellants, and explosives, and has attracted a great deal of attention because of its interesting physical and chemical properties. The absorption spectra and photochemistry of nitromethane have been studied extensively; however, the photodissociation dynamics of this simplest nitroalkane is still not clear due to the complication induced by its complex electronic structure. Studies of the spectra and photochemistry of nitromethane are briefly summarized below.

The absorption spectrum of liquid phase nitromethane has been investigated in the early of 1900s,¹⁻⁴ and is characterized by two regions of continuous absorption: a weak one with a maximum at about 300 nm, and a strong one starting from 250 nm and extending toward shorter wavelength. Two decades later, Thompson and Purkis⁵

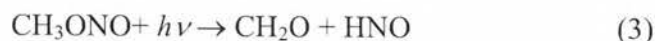
revealed that the absorption of nitromethane in the gas phase starts from 304 nm and continues beyond 180 nm with a subsidiary minimum at 245 nm, which is in general agreement with Hirschlaff and Norrish's observations.⁶ In the following years, the weaker absorption region was investigated extensively and found to peak near 276 nm.⁷⁻⁹ More recently, Loos and co-workers¹⁰ showed that the absorption spectra of gas phase nitromethane in the ultra-violet spectral region consist of two electronic bands: a strong band centered at 198 nm, which was first observed by Nagakura and assigned to a $\pi^* \leftarrow \pi$ transition localized on the NO₂ moiety,¹¹ and a much weaker band centered at 270 nm, which was assigned to a $\pi^* \leftarrow n$ transition by Bayliss and McRae.¹² More information about other excited states are provided by electron impact spectra,^{13,14} and photoelectron spectra.¹⁵

In the early stages of the study of the decomposition of nitromethane, reaction (1) shown below has been suggested to be the primary process for the photolysis of nitromethane by Hirschlaff *et al.*⁶ and Christie *et al.*¹⁶



Hirschlaff and Norrish performed a preliminary study of the decomposition of nitromethane in the gas phase using radiation of 300 to 200 nm. Their results show that the decomposition products can be interpreted quantitatively as resulting from reaction (1) followed by a secondary reaction of decomposition and oxidation by nitrosyl hydride (HNO) radicals. Christie and co-workers proposed that the same molecular fragmentation process is involved in the primary process of photolysis of nitromethane based upon the fact that the yield of formaldehyde is unaffected by the addition of nitric oxide.

Although Brown and Pimentel¹⁷ have also observed the HNO radical as one of the primary products from the photolysis of nitromethane in solid argon at 20 K and 240-360 nm radiation, they suggest that the photolysis of nitromethane in matrix isolation proceeds in two steps,



Here the nitro-nitrite isomerization is the primary process.

The nitro-nitrite isomerization process has been experimentally proven to be a competitive process with the rupture of C-NO₂ bond by Wodtke and co-workers¹⁸ in their IR multiple photon dissociation studies of nitromethane.

In order to explain the high yield of nitrosomethane in their study of the photolysis of nitromethane in the liquid phase at 254 nm, Cundall and co-workers¹⁹ suggest that an oxygen atom elimination process might be involved in the primary process:



Recently, Park and co-workers²⁰ have studied the dynamics of oxygen atom elimination in the gas-phase photolysis of nitromethane using two UV photodissociation laser wavelengths - 248 and 266 nm - at room temperature. They concluded that at both photolysis wavelengths oxygen atoms are produced mainly via an indirect predissociation mechanism, but at 248 nm there is an additional contribution from a direct predissociation mechanism.

Based on the observation of OH radicals with a quantum yield of 0.004 under collision-free conditions, an OH formation pathway in the photolysis of nitromethane at

266 nm has been suggested by Zabarnick *et al.*²¹ Greenblatt *et al.*,²² however, only observe the OH radical from photolysis of nitroalkanes with β - or γ -hydrogen through a five-membered ring intermediate at 282 nm. They did not detect any OH production from nitromethane.

Beyond the above different dissociation mechanisms, rupture of the C-NO₂ bond under photolysis conditions is suggested as the main primary process of photolysis of nitromethane by several authors:²³⁻²⁷



McGarvey and McGrath,²⁸ and Napier and Norrish²⁹ have confirmed reaction (5) as the main primary process in the photodissociation process by observation of the strong absorption spectrum of the methyl radical immediately after flash photolysis (μs) of nitromethane. In both experiments, the formation of methyl nitrite is proposed to be a result of the recombination of methyl radical and nitrogen dioxide. Honda *et al.*³⁰ have determined the quantum yields of the main products methyl nitrite, formaldehyde, nitrosomethane, and NO from the photolysis of nitromethane in gas phase at 313 nm, 55⁰C, and suggest that both reactions (1) and (5) are the primary processes of nitromethane photo-decomposition based on the dependence of product quantum yields on the pressure of quenching gases. In addition, Bielski and Timmons³¹ detected the ESR spectra of the methyl radical and nitrogen dioxide during photolysis of nitromethane at 77 K. Colles and co-workers³² utilized optoacoustic detection to provide the first spectral identification of the NO₂ fragment from continuous photolysis of nitromethane. Spear and Brugge³³ observed vibrationally excited NO₂ from photodissociation of nitromethane at 252.2 nm by laser induced fluorescence.

The dynamics of the photodissociation of nitromethane after the excitation of the $\pi^* \leftarrow n$ transition near 270 nm in the picosecond time regime have been measured by Schoen *et al.*³⁴ and Mialocq *et al.*³⁵ Both groups observed ground state NO₂ fragments with high quantum yield within 5-6 ps after absorption of a single photon near 270 nm supporting their conclusion that excitation of the $\pi^* \leftarrow n$ transition near 270 nm results in dissociation predominantly via reaction (5). One exception is that, in a cross laser-molecular beam study of nitromethane, Kwok *et al.*³⁶ found that the excitation of nitromethane at 266 nm did not yield dissociation product under collision-free conditions.

Excitation of nitromethane in the $\pi^* \leftarrow \pi$ transition also gives reaction (5) as the primary process.³⁷⁻⁴⁰ Blais³⁷ determined the dissociation cross section of nitromethane at 193 nm to be $1.7 \times 10^{-17} \text{ cm}^2$ with near unity quantum yield. Butler *et al.*³⁸ have investigated the dissociation of nitromethane following the excitation of the $\pi^* \leftarrow \pi$ transition at 193 nm by product emission spectroscopy and molecular beam photofragment translational energy spectroscopy. For the first time they suggested that there are two distinct mechanisms by which the methyl radical and nitrogen dioxide are produced. The dominant mechanism produces vibrationally excited NO₂ in the first ²B₂ electronic state, much of which unimolecularly dissociates to NO and O atom. The minor mechanism produces NO₂ in a different excited state which could efficiently absorb a second 193 nm photon to further dissociate to NO and O atom. These mechanisms are further confirmed by Moss *et al.*³⁹ through observation of the production of two NO electronic states (X and A) and the appearance of two peaks in the translational energy distributions of CH₃ and O fragments from 193 nm photolysis

of nitromethane. According to the polarized emission spectra from photodissociation of nitromethane excited at 200 and 218 nm, Lao *et al.*⁴⁰ suggested that the minor mechanism generates NO₂ in the second ²B₂ electronic state from the ¹B₂ surface of nitromethane. A recent theoretical calculation showed, however, that the NO₂ from the major and minor channels should be assigned as (1 ²B₁) and (1 ²A₂), rather than (1 ²B₂) and (2 ²B₂).⁴¹

In a brief summary, inconsistencies still exist for the photodissociation mechanism of nitromethane, although it has been investigated for decades. HNO elimination, nitro-nitrite isomerization, O atom elimination, OH formation, and C-NO₂ bond rupture have all been suggested to be the primary process for the photodissociation of nitromethane under admittedly different experimental conditions, such as different phases, different temperatures, and different photodissociation wavelengths. Among these different mechanisms, the formation of NO₂ after C-NO₂ bond rupture has been the best accepted mechanism. The dynamics for the NO₂ formation following the $\pi^* \leftarrow \pi$ excitation of nitromethane has not been measured to date, however. Although only two groups have tried to detect the OH radical from the photolysis of nitromethane, the final conclusions about OH radical formation are completely contrary: one group²¹ did observe the OH radical with low quantum yield, while the other²² did not. Moreover, several groups^{34,35} observed NO₂ as a major dissociation product from photolysis of nitromethane after $\pi^* \leftarrow n$ excitation at relatively high pressure and room temperature, Kwok *et al.*³⁶ did not observe any dissociation product from the excitation of nitromethane at 266 nm under collision-free conditions. Based on these issues, we investigate the photodissociation of nitromethane at different

wavelengths under different conditions so that we can compare our results with previous experiments to make as complete interpretation as possible for the photodissociation of nitromethane at the ($n\pi^*$) and ($\pi\pi^*$) excited electronic states from an experimental point of view.

The present chapter discusses the dynamics of the photolysis of nitromethane at two laser wavelengths (226 and 271 nm), which correspond to the $\pi^* \leftarrow \pi$ and the $\pi^* \leftarrow n$ transitions of nitromethane, respectively. The study employs both nanosecond and femtosecond pump-probe techniques combined with time of flight mass spectrometry (TOFMS) and laser induced fluorescence (LIF) spectroscopy. Photodissociation of nitromethane following $\pi^* \leftarrow \pi$ excitation has been investigated under both collisionless (in ionization/excitation region) and collisional (inside a quartz capillary) conditions. For comparison, some experiments at 193 nm excitation have been repeated under similar experimental conditions as those for 226 nm excitation. In nanosecond 226 nm ($\pi^* \leftarrow \pi$ excitation) laser experiments, the NO, CH₃ and OH molecules are observed as dissociation products under both collisionless and collisional conditions, and the CH₃O species is only observed as a dissociation product under collisional conditions. Although the NO₂ product has not been directly observed in these experiments, we can still conclude that the C-NO₂ bond rupture should be the primary process of the photolysis of nitromethane at 226 nm based on the analysis of resonance enhanced multiphoton ionization (REMPI) spectra for the NO molecule and the direct observation of the CH₃ product. Moreover, the direct observations of CH₃, NO₂ and NO fragment ions without parent ion signal in femtosecond 226 nm excitation experiments further confirm that NO₂ elimination is the primary process of the photolysis of

nitromethane at this wavelength. The observation of the OH radical with weak signal intensity in both nanosecond and femtosecond experiments indicates the OH radical formation should be a minor dissociation channel for nitromethane at 226 nm. Additionally, the observation of CH₃O species under collisional conditions rules out the direct nitro-nitrite isomerization mechanism, but confirms that recombination of the CH₃ and NO₂ leading to the formation of methylnitrite does occur in the presence of collisions. The photodissociation dynamics of nitromethane at 226 nm excitation is determined to be faster than our laser pulse duration (180 fs). In nanosecond 271 nm ($\pi^* \leftarrow n$ excitation) laser experiments, pump-probe experiments are performed to detect potential dissociation products, such as CH₃, NO₂, CH₃O and OH; however, none of them is observed. In femtosecond 271 nm laser experiments, the nitromethane parent ion is observed with major intensity, together with CH₃, NO₂ and NO fragment ions with minor intensities. Pump-probe transients for both nitromethane parent and fragments ions at 271 nm excitation and 406.5 nm ionization display a fast exponential decay with a constant time of 36 fs, which we suggest to be the lifetime of the excited ($\pi\pi^*$) state of nitromethane. Combined with the 271 nm nanosecond pump-probe experiments, in which none of the CH₃, NO₂, CH₃O or OH fragment is observed, we suggest that all the fragment ions generated in 271 nm femtosecond laser experiments are derived from the parent ion, and dissociation of nitromethane from the ($n\pi^*$) excited electronic state does not occur in a supersonic molecular beam under collisionless conditions.

3.2 Experimental Procedures

Detailed experimental procedures for nanosecond REMPI spectroscopy, laser induced fluorescence spectroscopy, and femtosecond laser pump-probe spectroscopy, have been described elsewhere.⁴²⁻⁴⁵ Briefly, the experimental setup consists of laser systems with both nanosecond and femtosecond time resolutions, a supersonic jet expansion nozzle, a time of flight mass (TOFM) spectrometer, and a laser induced fluorescence (LIF) spectrometer. For the nanosecond laser experiments, the photolysis of the nitromethane at 226 nm excitation is performed at two different positions: one is in a quartz capillary attached to the supersonic jet expansion nozzle representing collisional conditions before molecular beam expansion; the other is in the ionization/excitation region of the TOFM/LIF spectrometer representing collisionless conditions after molecular beam expansion. The photolysis of nitromethane at 271 nm excitation is only performed in the ionization/excitation region under collisionless conditions.

In the 226 nm excitation experiments, a pump laser beam at 226 nm is used to initiate the dissociation of nitromethane, and a probe beam with about 50 ns or 50 μ s delay time depending on where the photolysis occurs, is employed to detect photodissociation products. In the case for which both pump and probe beams are at the same wavelength (NO product detection) only a single beam is employed. The NO product is detected by (1+1) REMPI through $[A^2\Sigma^+ \leftarrow X^2I]$ transition at 226 nm and the CH₃ product is detected by (2+1) REMPI through $[4p^2A'' \leftarrow X^2A'']$ resonance transition at 286 nm. The (0-0) and (0-1) rovibronic excitation spectra of fragment NO are obtained by scanning the laser wavelength around 226 and 236 nm, respectively. In

addition, two other wavelengths at 303, and 308 nm are employed to probe CH₃O [$A^2A_1 \leftarrow X^2E, 2_0^1$] and OH [$A^2\Sigma^+ (v'=0) \leftarrow X^2\Pi (v''=0)$] species through LIF spectroscopy. In the nanosecond 271 nm experiments, the pump beam at 271 nm is used to excite the nitromethane molecule through the $\pi^* \leftarrow n$ transition, and a second beam at 532, 303, 286 or 308 nm is used to probe the potential NO₂, CH₃O, CH₃ or OH product.

The UV laser pulse used in the nanosecond laser experiments is generated by a pulsed dye laser, pumped by the second harmonic (532 nm) of a Nd:yttrium aluminum garnet laser's fundamental output (1.064 μ m), in conjunction with a nonlinear wavelength extension system. In order to determine the dependence of the rotational temperature of fragment NO on the UV laser beam intensity, a 226 nm pulse energy of 16 - 300 μ J/pulse is used to provide laser beam intensities (I) $\sim 6.5 \times 10^6$ to 1.2×10^8 W/cm² for an 8 ns pulse duration at a focused beam diameter of 0.2 mm. Up to 2 mJ energy of 271 nm has been used in the nanosecond LIF experiments. The pulse energy for different probe laser wavelengths varies from several hundreds micro joule up to 5 mJ. Additionally, an excimer laser centered at 193 nm and a vacuum ultraviolet laser centered at 118 nm have also employed as pump and probe beams, respectively, to verify the fragments from photodissociation of nitromethane at 193 nm.

For fs 226 nm pump-probe experiments, a single laser beam is equally split into pump and probe beams, and at 271 nm laser wavelength, the 271 nm beam is used as the pump pulse, and a second beam centered at 406.5 nm is used as the probe pulse. Sample molecules are excited by the pump beam and dissociate according to their dissociation dynamics. Dissociation products are subsequently ionized by the delayed

probe beam and detected via TOFMS. By delaying the probe beam with respect to the pump beam, product appearance times can be determined. Three cases could be involved in the pump-probe transient analysis depending on different dynamic processes. First, if the dissociation dynamics are much slower than the laser pulse duration, the pump-probe transients for dissociation products should show a buildup then a plateau because of the relatively long lifetime of the fragments. In this case, we can extract the kinetic time employing a single exponential buildup function. Second, if the dissociation dynamics are much faster than the laser pulse duration, the pump beam can not only dissociate the sample molecule, but also ionized the dissociation products via non-resonance multiphoton ionization. In this case, rather than a buildup transient for the fragment, an auto-correlation (same frequency) or cross-correlation (different frequency) transient for the laser pulses would be observed, and a upper limit of the dynamic process can be determined to be faster than the laser pulse duration. Third, if sample molecule does not dissociate following excitation by the pump beam, and the probe beam ionizes the sample molecule from its excited state, then the lifetime of the excited state of the sample molecule can be extracted from the pump-probe transient using single exponential decay function. Cases (2) and (3) are used to analyze the pump-probe transients following 226 and 271 nm excitation, respectively.

The femtosecond laser light is generated by a femtosecond laser system consisting of a self-mode-locked Ti:Sapphire oscillator (KM Labs), a home-made ring cavity Ti:Sapphire amplifier, and a commercial traveling wave optical parametric amplifier of super fluorescence (TOPAS, Light Conversion) system. The 226 nm laser pulse is the deep UV output from the TOPAS system which is pumped by the

fundamental wavelength of 813 nm. Pulse duration of the deep UV laser pulse is measured to be 180 fs using a self-diffraction (SD) autocorrelator and off-resonance two-photon absorption of the furan molecule.⁴⁶ Typical pulse energy of the deep UV output is ~ 1 μ J/pulse. For one-color time resolved investigations, the energy of pump and probe pulses is kept at an optimum value of ~ 200 nJ/pulse ($I \sim 5.66 \times 10^8$ W/cm²) to improve signal-to-noise ratio and to avoid uncontrolled fragmentation due to multiphoton absorption by the parent molecule. The 406.5 and 271 nm laser beams, which are generated by two non-linear β -BaB₂O₄ (BBO) crystals, are the second and third harmonics of the fundamental 813 nm femtosecond laser pulse. The energies of 406.5 and 271 nm laser pulses are about 15 and 2 μ J, respectively. The cross-correlation of the two beams is measured via the two photon non-resonance ionization of benzene molecule (as shown in Fig. 3.1), which yields a time duration of the laser pulse of about 170 fs using the relation of $\tau_L = \frac{\sqrt{2}}{2}$ [full width at half maximum] (FWHM).

The experiment is run at a repetition rate of 10 Hz. The timing sequence for the pulsed nozzle, excitation laser, and ionization laser is controlled by a time delay generator (SRS DG535). The molecular beam is perpendicularly crossed by a UV laser beam that is focused to a spot size of about 0.2 mm at the ionization/excitation region of the spectrometer. A background pressure of 1×10^{-5} Torr is maintained in the vacuum chamber during the experiment. Ion signals are detected by a microchannel plate detector (MCP), and fluorescence signal is collected by a photomultiplier tube (PMT). Signals are recorded and processed on a personal computer using a box car averager (SRS SR 250) and an analog-to-digital conversion (ADC) card (Analog Devices RTI-800). For femtosecond time resolved experiments, the delay time between the pump

and probe beam is controlled by a microtranslation stage (Thorlabs: LNR50SEK1) with a step size of 13 fs. Each point on the pump-probe transient spectrum corresponds to an average intensity resulting from 100 laser shots.

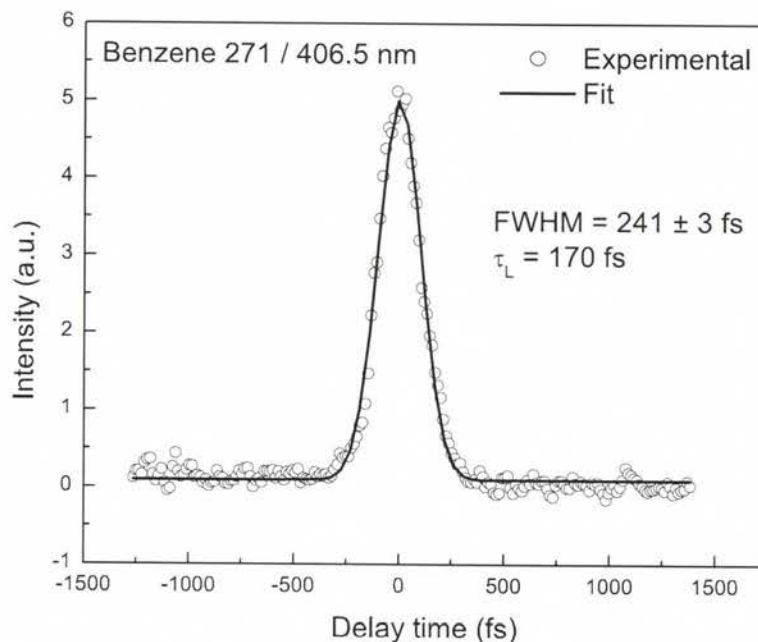


Figure 3.1: Measurement of femtosecond laser pulse cross-correlation between 271 nm (pump) and 406.5 nm (probe) wavelengths using off-resonance absorption of the benzene molecule. The laser pulse duration is determined to be 170 fs ($\tau_L = \text{FWHM} / \sqrt{2}$).

A commercial nitromethane sample (Aldrich) is used in these experiments without additional purification. The vapor phase nitromethane molecules at room temperature are carried into the nozzle by helium carrier gas under a pressure of 30 psig through a glass vial. An NO_2 sample at a concentration of 0.01% is premixed with helium and 10% O_2 , for use in spectrum comparison and system test.

3.3 Results and Discussions

A. Photodissociation of nitromethane following the $\pi^* \leftarrow \pi$ excitation

Photolysis of nitromethane following the $\pi^* \leftarrow \pi$ excitation at 226 nm is investigated under both collisionless and collisional conditions. In both cases, the gas phase nitromethane molecule is excited by absorbing a single 226 nm photon, which corresponds to the $\pi^* \leftarrow \pi$ strong absorption transition around 198 nm, and then dissociates into products along different dissociation pathways. The dissociation products after the $\pi^* \leftarrow \pi$ excitation are probed by either the same laser or a second time delayed laser beam at different wavelength. In order to clarify which one of the possible dissociation channels of C-NO₂ bond rupture, OH formation, O atom elimination, or the nitro-nitrite isomerization is open at this electronic excitation, the CH₃, NO₂, NO, OH, CH₃O, and CH₃NO species have been probed by either TOFM or LIF spectroscopy. Since the 193 nm excitation of nitromethane belongs to the same $\pi^* \leftarrow \pi$ absorption transition, some of the experiments at this wavelength are repeated under similar conditions to those at 226 nm excitation; which leads to a close comparison between these two wavelengths for the same absorption excitation. The results for each possible dissociation mechanism are presented and discussed in following sub sections.

1. Observation of CH_3 , NO and NO_2 fragments

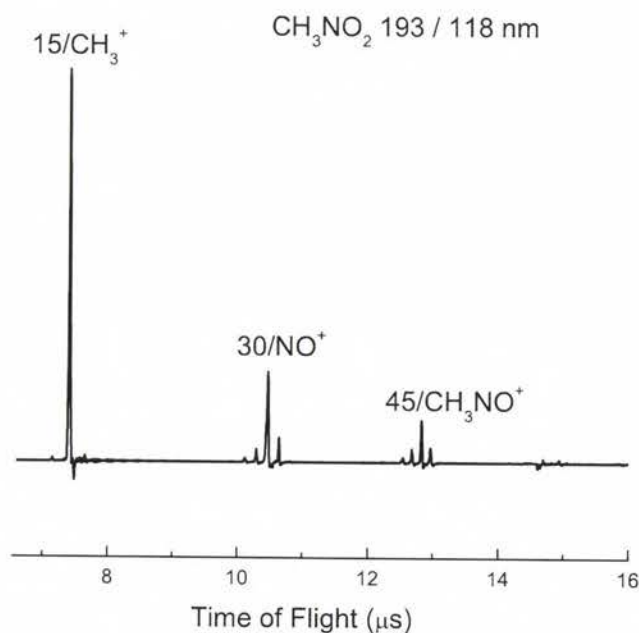


Figure 3.2: Mass spectrum of the photodissociation of nitromethane following excitation of $\pi^* \leftarrow \pi$ transition using 193 nm nanosecond laser pulses. A nanosecond 118 nm laser pulse is employed to ionize the dissociation products. CH_3 , NO and CH_3NO are apparent product peaks, small peaks around NO and CH_3NO are impurity signals from 193 nm ionization.

The primary fragmentation products after the $\pi^* \leftarrow \pi$ excitation of nitromethane are suggested to be CH_3 and NO_2 .³⁸ The NO_2 fragment in the 1^2B_2 excited state can automatically dissociate into NO (X) and O (^3P) as secondary products when the excitation photon energy is high enough. As illustrated in the mass spectrum (Fig. 3.2) obtained by 193 nm excitation of nitromethane in the ionization region of the TOFM spectrometer employing 118 nm ionization of dissociation products, the CH_3 mass channel shows much greater intensity than that of the NO mass channel, produced from the dissociation of the NO_2 fragment. This confirms that the C- NO_2 bond rupture is the

main primary process for the dissociation of nitromethane following the $\pi^* \leftarrow \pi$ excitation, and that the NO_2 molecule should be the precursor for the NO product. The third peak (mass channel 45 amu) is given by O atom elimination from nitromethane and will be discussed later. Several other weak peaks around the three major peaks are impurity signals derived from 193 nm ionization.

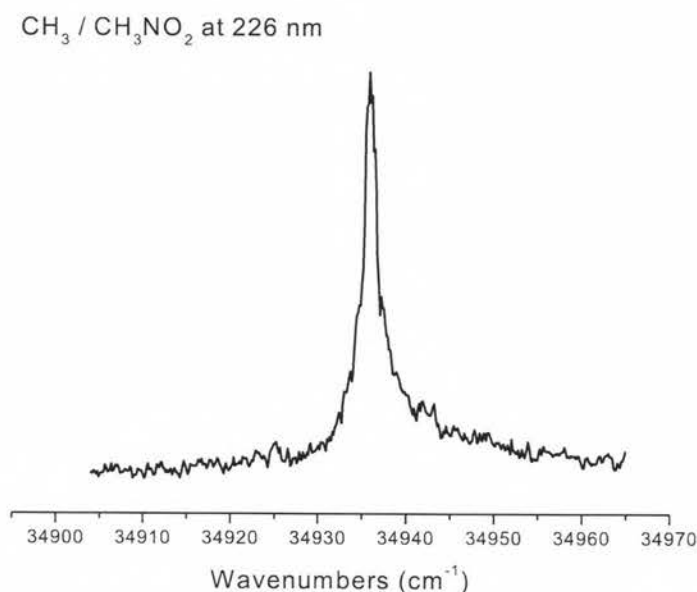


Figure 3.3: Two-color (286 and 118 nm), (2+1) REMPI of the CH_3 , following $[4p^2A'' \leftarrow X^2A']$ electronic transition, produced from photolysis of nitromethane at 226 nm

For 226 nm excitation of nitromethane in the ionization region, the 118 nm ionization detection scheme can not probe the dissociation products due to the low energy of both 226 and 118 nm laser pulses. Therefore, REMPI is employed to probe both CH_3 and NO products from the photolysis of nitromethane at this wavelength (226 nm). The REMPI spectrum of CH_3 radical is presented in Fig. 3.3. This spectrum is generated by one color (286 nm), two photon, resonance absorption from the CH_3 ground electronic state to its 4p Rydberg state $[4p^2A'' \leftarrow X^2A']$, and a third photon

(118 nm) is required to ionize the CH_3 radical from the excited state to CH_3^+ . The only distinguishable feature in this spectrum is a very strong, sharp Q branch with no resolved rotational structure. The rotational temperature of CH_3 radical has been determined to be 200 K with large uncertainty by Moss and his co-worker in their 193 nm excitation experiment.³⁹ This confirms that the CH_3 product from $(\pi\pi^*)$ excited state decomposition of nitromethane is relatively rotationally cold.

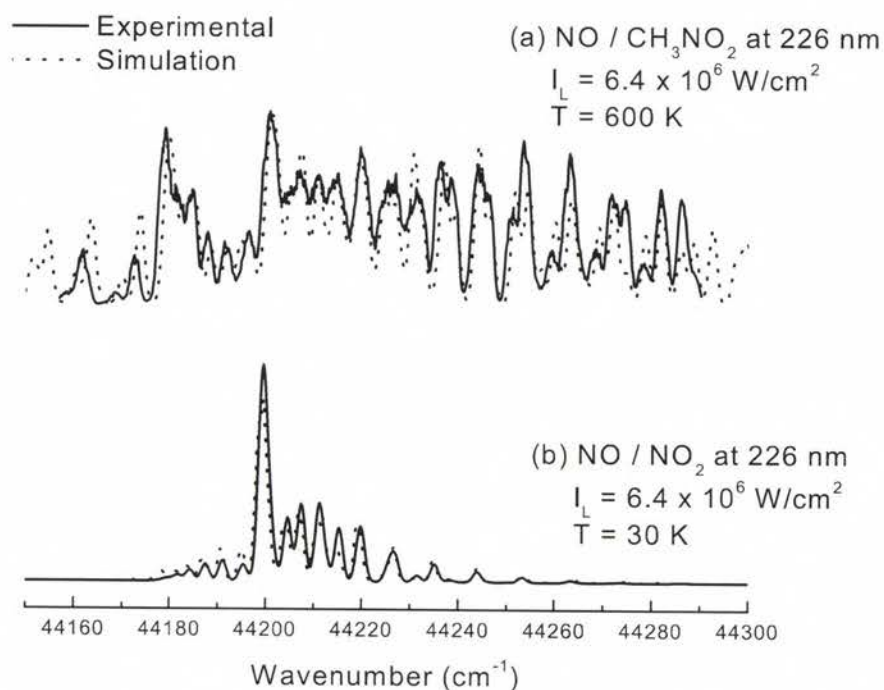


Figure 3.4: One-color (226 nm) REMPI of the NO [$A^2\Sigma^+ (v'=0) \leftarrow X^2\Pi (v''=0)$] product from photolysis of nitromethane (a), and NO_2 (b) at 226 nm. The solid lines are experimental measurements, the dotted lines are simulations by Boltzmann population distributions, which produce rotational temperatures of 600 and 30 K for the NO product from nitromethane and NO_2 , respectively, at a laser intensity of $6.4 \times 10^6 \text{ W/cm}^2$

The NO product in its ground electronic state is probed at the same wavelength (226 nm) through its $A^2\Sigma^+ (v'=0) \leftarrow X^2\Pi (v''=0)$ transitions. Figure 3.4 (a) shows a one color REMPI spectrum of the NO product from photodissociation of nitromethane at

226 nm. The spectrum is rotationally resolved and most of the recorded features belong to the $^2\Pi_{1/2}$ component of the ground electronic state. The most intense feature in this spectrum can be assigned as the ($Q_{11} + P_{12}$) band head of the (0-0) vibronic band, and the less intense features are due to other rovibronic transitions.^{47,48} Spectral simulations based on the Boltzmann population distribution produces a rotational temperature of 600 K for the NO product under the laser intensity used for recording this spectrum. In addition to the (0-0) vibronic band, the (0-1) vibronic band is also observed with similar rotational distribution. The hot rotational distribution of NO product from photodissociation of nitromethane after the $\pi^* \leftarrow \pi$ excitation at 226 nm is in good agreement with Moss *et al.*'s observation,³⁹ from which they determined the rotational temperature of the NO product from 193 nm photolysis of nitromethane to be 1000 K.

According to the energy level diagram for photodissociation of nitromethane following the $\pi^* \leftarrow \pi$ excitation,³⁹ however, a single 193 nm photon (6.4 eV) has enough energy to produce the NO product in its ground electronic state through an electronically excited NO₂ intermediate. This process needs at least 5.8 eV energy, but a single 226 nm photon (5.5 eV) has only enough energy to produce an excited NO₂ (1^2B_2) molecule, which does not have enough internal excitation energy to decompose further into an NO product. Therefore, the NO₂ product in its 1^2B_2 excited state needs to absorb a second photon from the 226 nm excitation laser to be dissociated into an NO product, which displays relatively higher vibrational temperature (both $v'' = 0$ and 1 are observed) and lower rotational temperature (600 K) than the NO from 193 nm excitation, for which only $v'' = 0$ is observed and the rotational temperature is about 1000 K.

For comparison purposes, the REMPI spectra of the NO product from photodissociation of NO₂ molecule at 226 nm are presented in Fig. 3.4 (b). Both spectra are obtained under similar low laser intensity. A single 226 nm photon excites NO₂ to its 2²B₂ state⁴⁹ with high vibrational excitation. The excited NO₂ molecule then dissociates into an NO in its ground electronic state and O in its ¹D excited state.⁵⁰ The NO product from this NO₂ excited state (2²B₂) shows a rotational distribution of about 30 K, much colder than the NO product from the NO₂ (1²B₂) produced in the photolysis of nitromethane. Since the NO₂ molecule from both the dissociation of nitromethane at 226 nm and the NO₂ gas sample must absorb one 226 nm photon to dissociate into an NO product, based on the large rotational temperature difference of the NO product, one can conclude that the NO₂ product from the dissociation of nitromethane is not in its ground electronic state. The ground state NO₂ product is also tried probed by LIF spectroscopy through 532 nm excitation after the dissociation of nitromethane at 226 nm. No fluorescence signal is observed from the NO₂ molecule, which further confirms that most of the NO₂ products generated from nitromethane are in the excited electronic state (1²B₂).

The spectrum of the NO product from photolysis of nitromethane probed at different laser (226 nm) intensities is shown in Fig. 3.5. Except for the distortion due to power broadening, all spectra show a similar pattern, which produces about the same rotational temperature of 600 K for the NO product. Thus we conclude that the rotational temperature of the NO product from photodissociation of nitromethane at 226 nm excitation is laser intensity independent. Similar REMPI spectra of the NO product from photodissociation of NO₂ with different laser beam intensities are shown in Fig.

3.6, in which one can find that the rotational temperature of the NO product from NO₂ molecule is laser intensity dependent. At the maximum laser intensity used in these experiments, a rotational temperature of about 100 K is observed, much hotter compared to the NO product produced at low laser intensity, which is about 30 K.

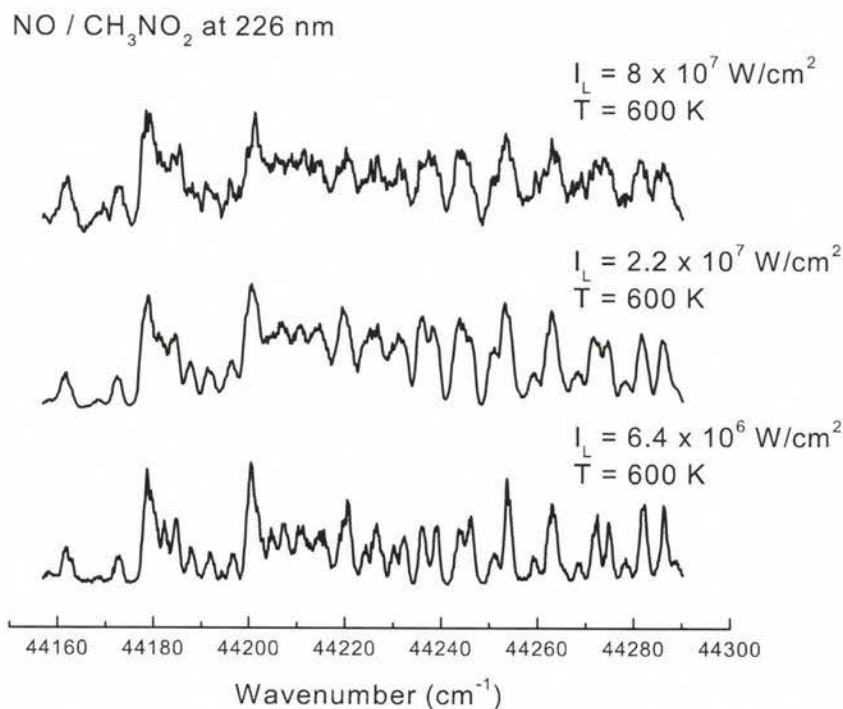


Figure 3.5: Comparison of the one-color REMPI spectra of the NO [$A^2\Sigma^+$ ($v'=0$) $\leftarrow$ $X^2\Pi$ ($v''=0$)] product from photolysis of nitromethane at different intensities of 226 nm laser pulses.

At high laser intensity, NO production from the dissociation of NO₂ at 226 nm has been fully investigated.⁵¹ The conclusion is that four-photon absorption process can occur for the fragmentation of NO₂ and the excitation and ionization of NO product at high laser intensity. Two photons excite the NO₂ molecule, and another two excite and ionize the NO (X) product. Two possible excited states of the NO₂ have been suggested as candidates for the NO₂ dissociative states after absorption of two photons at 226 nm:

a Rydberg state at 10.85 eV and an ion-pair state. For either state, the dissociation dynamics can produce an NO(X) predominantly with hot rotational and vibrational energy distributions. Since two different pathways are involved in the dissociation of NO₂ molecule at high laser intensity, the rotational distribution of the NO product at different laser intensity should be the superposition of the NO product from both dissociation pathways, which results in different rotational temperatures of the NO product at different laser intensities.

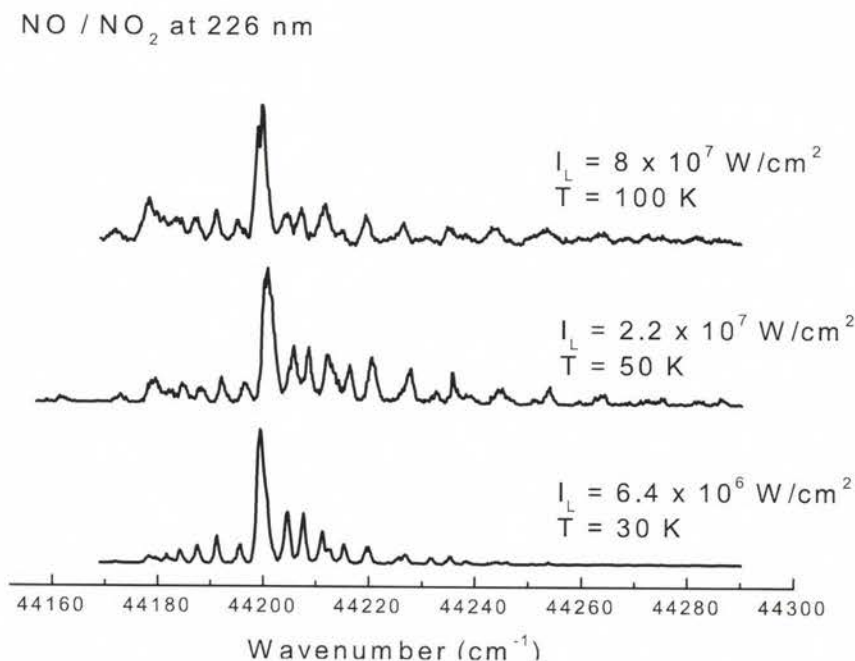


Figure 3.6: Comparison of the one-color REMPI spectra of the NO [$A^2\Sigma^+(v'=0) \leftarrow X^2\Pi(v''=0)$] product from the photolysis of NO₂ at different intensities of 226 nm laser pulses

Although two different channels for the production of NO₂ in two different excited state (1^2B_2 and 2^2B_2) have been proposed in the dissociation of nitromethane at 193 nm,^{38,40} only the major channel which produces NO₂ in 1^2B_2 state is open at 226 nm excitation because the CH₃ + NO₂ (2^2B_2) dissociation limit is about 19 kcal/mol

higher than the photon energy of 226 nm wavelength. As mentioned above, the NO_2 (1^2B_2) from the 226 nm photodissociation of nitromethane absorbs a second photon, then dissociates into an NO ($X^2\Pi$) product with hot rotational and vibrational distributions. This is different from the NO_2 (2^2B_2) prepared by absorption of a 226 nm photon by NO_2 gas, which is highly vibrationally excited and can dissociate into NO (X) with cold rotational and vibrational distributions. Under high laser intensity irradiation, the NO_2 (2^2B_2) can easily absorb a second 226 nm photon and reach a Rydberg or ion pair state, then dissociate into NO (X) with a hot rotational distribution through a different channel. This could be a reasonable explanation for the different laser intensity dependence of the dissociation of nitromethane and NO_2 via 226 nm excitation. Moreover, the laser intensity independence of the NO product from nitromethane further confirms that the NO_2 product is not in its ground electronic state.

The TOFM spectrum of the photodissociation of nitromethane under femtosecond 226 nm irradiation is presented in Fig. 3.7. Three major mass channels with mass of 15, 30 and 46 amu, corresponding to CH_3 , NO, and NO_2 ions are observed after the photodissociation of nitromethane at this wavelength. Nitromethane parent ion is not observed. The linewidth for these three fragment mass peaks varies from 10 to 13 ns, which is the instrumental line width of the TOFMS spectrometer. Since the CH_3 , NO_2 , and NO radicals are directly observed as photodissociation products from nitromethane following nanosecond 226 nm excitation, and the linewidth for the three fragment mass peaks is not broadened, we can conclude that the fragment ion signal is not from the fragmentation of nitromethane parent ion (not observed), but rather from the ionization of neutral dissociation products following $\pi^* \leftarrow \pi$ excitation. The direct

observation of CH_3 and NO_2 fragments further confirms that rupture of C- NO_2 bond should be the primary process for the photolysis of nitromethane after the excitation of $\pi^* \leftarrow \pi$ transition. NO is a secondary product from the unimolecular dissociation of the NO_2 fragment.

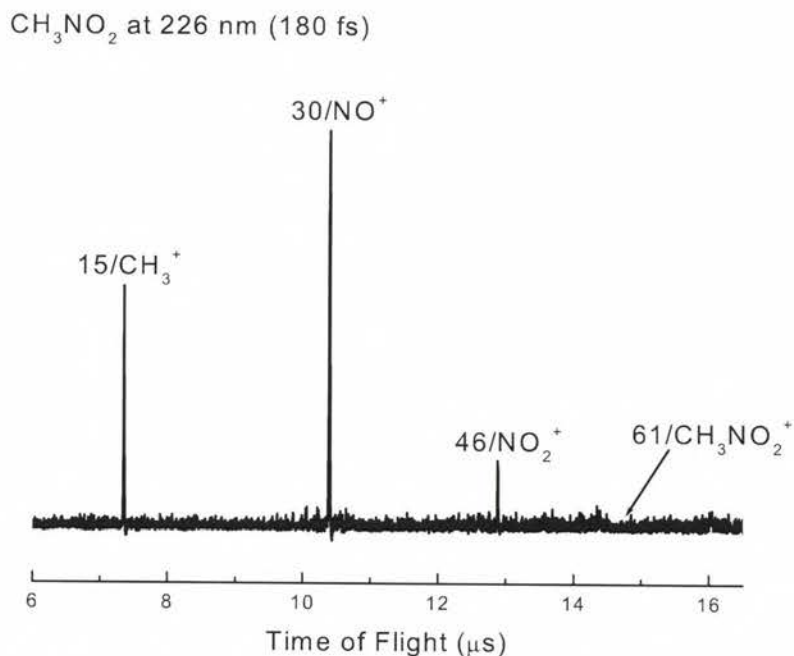


Figure 3.7: Mass spectrum of the photolysis of nitromethane following $\pi^* \leftarrow \pi$ excitation at femtosecond 226 nm. The parent ion at mass channel 61 amu is not observed.

In order to measure the dynamics of the formation of CH_3 and NO_2 fragments, a single 226 nm femtosecond beam is equally splitted into pump and probe beams with identical intensity. The nitromethane molecule is pumped to its excited state by absorbing a single photon from the pump beam, then dissociates into CH_3 and NO_2 products. The products are further excited and ionized by absorbing one or two photons from the probe beam. By scanning the delay time between the pump and probe beams, we should obtain transients illustrating the exponential buildup time of the fragments if

the dissociation dynamics of nitromethane is much slow compared to the time duration of our laser pulse. On the other hand, if the dynamics of the dissociation of nitromethane is much faster than the laser pulse duration, the pump beam can not only fragment the parent molecule, but also excites and ionizes the fragments by non-resonant two-photon absorption. In this case, we will not observe the buildup of the fragments, but an auto-correlation between the pump and probe beams near the zero delay time.

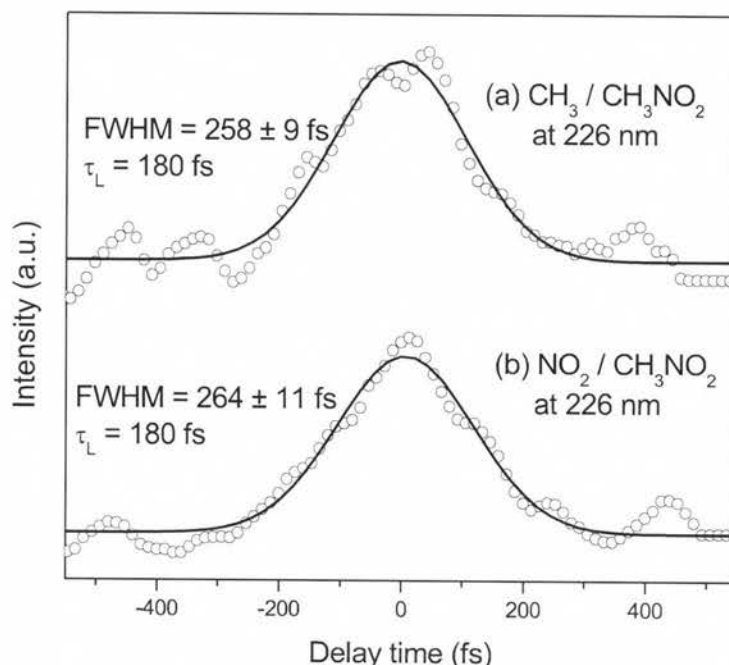


Figure 3.8: Femtosecond pump-probe transients for the CH_3 (a) and NO (b) fragments from the photolysis of nitromethane at 226 nm. Open circles are experimental measurements, solid lines are Gaussian fittings. Both transients show an auto-correlation of laser pulses with time duration of about 180 fs.

The pump-probe transients for the fragments CH_3 and NO_2 from the dissociation of nitromethane are shown in Fig. 3.8 (a) and (b). Rather than an exponential buildup for the transient fragments, both Figure 3.8 (a) and 3.8 (b) present

auto-correlation curves which can be fitted by a Gaussian pulse shape with time duration of 180 fs. Thus we conclude that the photodissociation of nitromethane at 226 nm in femtosecond time regime is faster than our laser pulse duration. To date, no direct dynamics measurement of the photodissociation of nitromethane following the $\pi^* \leftarrow \pi$ excitation has been reported.

2. Observation of CH_3NO

In Fig. 3.2, in addition to the CH_3 and NO products from the C- NO_2 bond rupture pathway, a third product CH_3NO with mass of 45 amu shows that O atom elimination also occurs after the $\pi^* \leftarrow \pi$ excitation of nitromethane. Compared to the signal intensity of CH_3 and NO products, the CH_3NO product displays relatively weak intensity, especially since some impurity signal is also present at this mass channel. The direct observation of a CH_3NO peak with weak intensity confirms that the O atom elimination should be one of the dissociation pathways for nitromethane following the $\pi^* \leftarrow \pi$ excitation with a small branching ratio. This observation is consistent with Park and co-workers' studies of photolysis of nitromethane at 248 nm, in which they observed some O atom intensity contributed from a direct predissociation mechanism.²⁰ Both Park's and our observations are different from Cundall and co-workers' results that a high yield formation of nitrosomethane is obtained from photolysis of nitromethane in liquid at 254 nm. The possible reason for the difference might be that intermolecular interactions of the excited nitromethane molecule in liquid play a role in the formation of nitrosomethane. Moreover, different wavelength excitations could also lead to different primary dissociation processes.

3. Observation of CH_3O radical

The nitro-nitrite isomerization mechanism has been determined to be the primary process by Brown and Pimentel in their photolysis of nitromethane in solid argon at 20 K and 240-360 nm radiation.¹⁷ Additionally, Wodtke and co-workers observed that the nitro-nitrite isomerization is competitive with the rupture of C-N bond in their IR multiphoton dissociation studies of nitromethane.¹⁸ On the contrary, several groups suggested that the methyl nitrite should be a result of the recombination of CH_3 radical and $\text{N}^{\sim}$ ^{28,29}

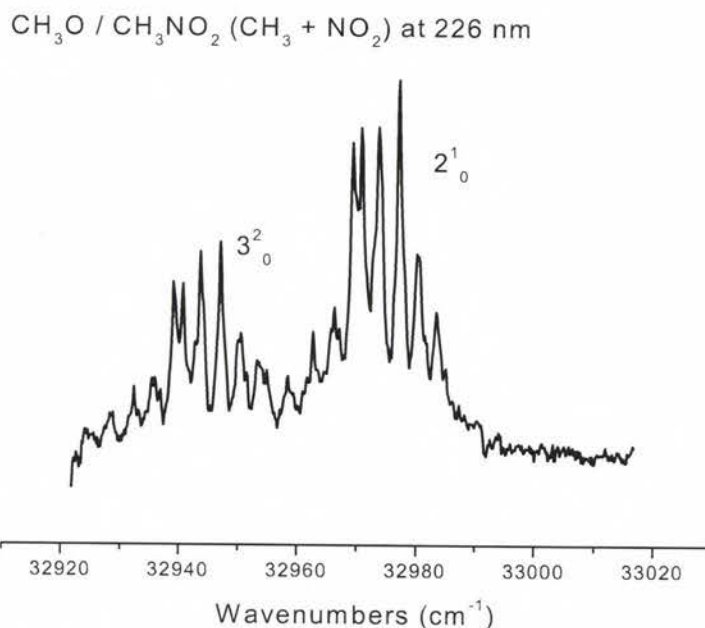


Figure 3.9: The LIF spectrum of CH_3O [$A^2A_1 \leftarrow X^2E$] product derived from recombination of CH_3 and NO_2 products from the photolysis of nitromethane at 226 nm in a quartz capillary (collisional conditions).

To confirm that the nitro-nitrite isomerization is one of the dissociation pathways for nitromethane following $\pi^* \leftarrow \pi$ excitation, the CH_3O radical is probed by LIF spectroscopy after the excitation of nitromethane at 226 and 193 nm in both the excitation region of the LIF spectrometer and in the quartz capillary attached to the

supersonic jet expansion nozzle. The fluorescence signal of the CH_3O product after the $A\ ^2A_1 \leftarrow X\ ^2E$ excitation can only be observed under collisional conditions when the photolysis of nitromethane is performed inside the quartz capillary. The excitation fluorescence spectrum of the CH_3O radical is illustrated in Fig. 3.9 for two transition bands (3_0^2 and 2_0^1) along with their rotational structures. No CH_3O radical signal is observed under collisionless conditions, but a relatively intense signal is observed for CH_3O under collisional conditions. Thus, formation of CH_3O is not directly by way of a nitro-nitrite isomerization mechanism, but as a result of recombination of the CH_3 and NO_2 species after the C-N bond rupture. This is in good agreement with McGarvey²⁸ and Napier's²⁹ suggestions. It also confirms that the NO product observed in the ionization/excitation region of the TOFM and LIF spectrometers is not from the isomerization intermediate (CH_3ONO), but from the secondary dissociation of NO_2 product. In addition, since Wodtke and co-workers observed the nitro-nitrite isomerization product from their IR multiphoton dissociation of nitromethane in its ground electronic state, we may infer that the nitro-nitrite isomerization mechanism takes place in the dissociation of nitromethane from the ground electronic state, but not from its excited electronic states (at least from $(\pi\pi^*)$ state).

4. Observation of OH radical

In gas phase photolysis of nitromethane, two groups tried to detect the OH radical as a dissociation product. Zabarnick and co-workers observed the OH radical with a quantum yield of 0.004 from photolysis of nitromethane at 266 nm;²¹ however, Greenblatt and co-workers did not observe the OH radical from their photolysis of nitromethane at 282 nm.²² The mechanism for the OH radical formation is not clear yet,

although Zabarnick pointed out that OH is generated via a mechanism not involving a five-membered ring formation. Thus, we search for an OH product by LIF spectroscopy following 226 nm excitation of nitromethane in both the excitation region of the LIF chamber (no collisions) and the quartz capillary attached to the nozzle (collisions). In the excitation region of the LIF spectrometer, a very weak fluorescence signal (a few mV) is observed by 308 nm probe laser through the OH [$A^2\Sigma^+ (v'=0) \leftarrow X^2\Pi (v''=0)$] transition.

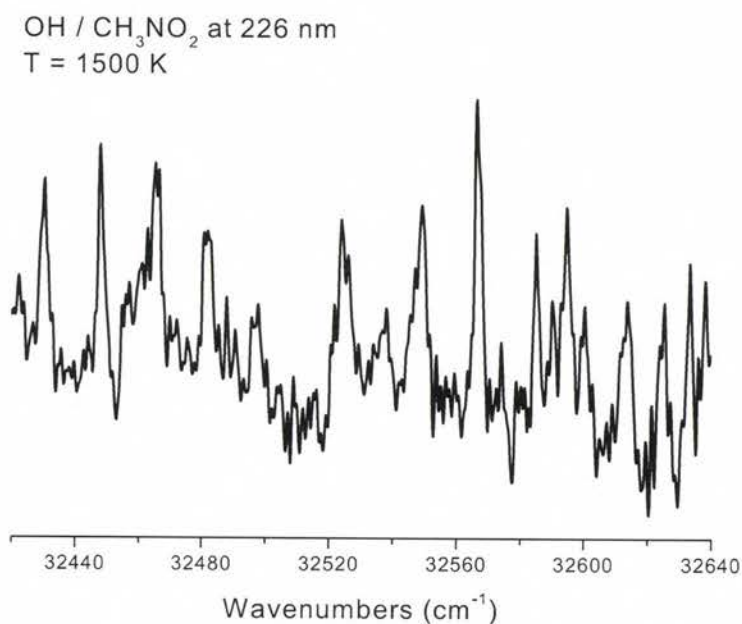


Figure 3.10: A portion of the LIF spectrum of OH [$A^2\Sigma^+ (v'=0) \leftarrow X^2\Pi (v''=0)$] product from the photolysis of nitromethane at 226 nm. The OH product has a 1500 K rotational population distribution.

The fluorescence excitation spectrum of OH is presented in Fig. 3.10, characterized by a very hot rotational spectral structure. Simulations based on a Boltzman population distribution give a rotational temperature for OH $X^2\Pi (v''=0)$ of 1500 K. The OH radical is also observed with relatively stronger intensity but much colder rotational distribution (30 K) after the photodissociation of nitromethane in the

quartz capillary. Supersonic expansion following formation of the OH radical inside the quartz capillary cools down the dissociation product (OH), and leads to the band head spectral line intensity increasing. At 193 nm excitation, in both the LIF excitation region and quartz capillary, the OH radical is also observed as a photodissociation product with similar rotational distribution to that at 226 nm excitation. The Franck-Condon factor for the (0–1) vibronic band of the OH radical is about ten times less than that of (0–0) band, based on the weak intensity of the (0–0) vibronic band, we do not expect to observe the (0–1) vibronic band of the OH radical transition in our experiments.

The mechanism for the OH radical formation from photolysis of nitromethane is not clear to date. Since the NO product is observed as a dissociation product above, it is very possible that both the NO and OH radicals are generated from an HONO intermediate formed through a five- or four-membered ring mechanism. To form a five-membered ring in a nitromethane molecule, nitro-nitrite isomerization should occur first. The nitro-nitrite isomerization mechanism is ruled out by the observation of CH₃O product under only collisional conditions, however. Therefore, if the OH radical is generated from secondary dissociation of HONO intermediate, the dissociation of nitromethane in the $\pi\pi^*$ excited electronic state should involve a four-membered ring formation mechanism. To insure that the NO product is not mostly from the secondary dissociation of an HONO intermediate, we also measured the NO fluorescence signal after the 226 nm excitation of nitromethane. The maximum signal intensity of NO fluorescence is about 1 V, and the LIF excitation spectrum of NO product shows a rotational temperature of about 600 K, which is similar to the REMPI spectrum of the

NO product. Based on the analysis of Frank-Condon factors and Boltzmann population distributions of NO and OH species, the signal intensity ratio between NO and OH radicals should be about 1:3 assuming both are derived from the same precursor. The signal intensity of NO is much greater than that of OH, and therefore we conclude that HONO formation is at most a minor channel for the photodissociation of nitromethane following $\pi^* \leftarrow \pi$ excitation, and the NO product is mostly derived from the secondary dissociation of the primary NO_2 product.

As discussed above, O atom elimination does occur following the $\pi^* \leftarrow \pi$ excitation of nitromethane. Thus, we can not rule out the formation of an OH radical through H atom extraction from methyl group of any possible dissociation products (such as CH_3 , CH_3NO , or even nitromethane) by O atom.

B. Photodissociation of nitromethane following the $\pi^* \leftarrow n$ excitation

Since both Shoen *et al.*³⁴ and Mialocq *et al.*³⁵ have reported ground state NO_2 as a major photodissociation product following $\pi^* \leftarrow n$ excitation of nitromethane by picosecond excitation at 266 nm at room temperature, nanosecond laser pump-probe experiments are carried out to detect the NO_2 product from photolysis of nitromethane at 271 nm excitation. A 532 nm laser beam is used as the probe beam, and the fluorescence signal from NO_2 gas after 532 nm excitation is shown in Fig. 3.11 under collisionless conditions. After a careful search for the NO_2 fluorescence signal following $\pi^* \leftarrow n$ excitation of nitromethane in the supersonic molecular beam at 271 nm, we did not observe any fluorescence signal through a pump-probe, collisionless detection scheme. This observation shows that NO_2 product is not generated at 271 nm excitation of nitromethane in the supersonic molecular beam under collisionless

conditions. Compared with Shoen and Mialoq's experimental conditions, the observation of the ground state NO_2 production in their experiments might be ascribed to high pressure and high temperature.

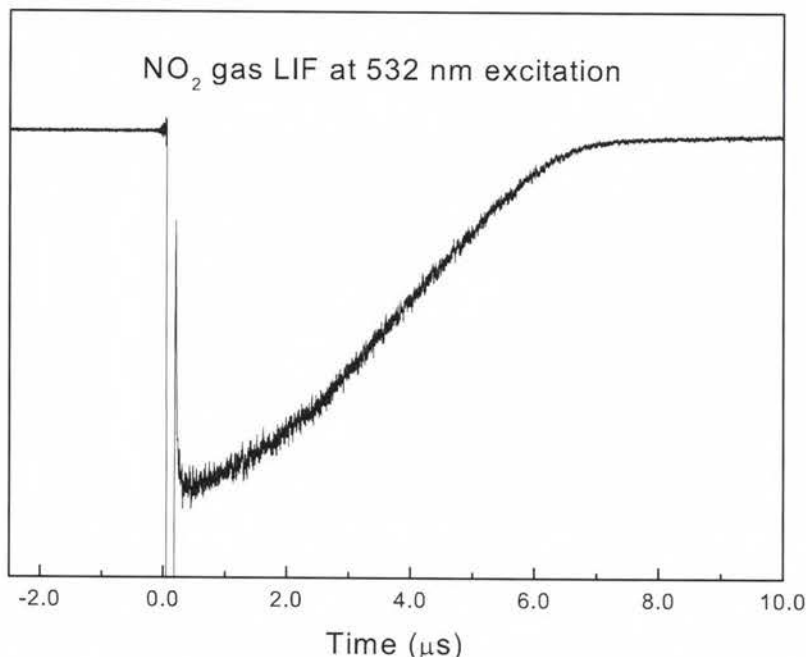


Figure 3.11: Fluorescence signal from excited NO_2 molecule at 532 nm excitation of NO_2 gas.

As mentioned above, the OH radical has been detected as a product through a minor dissociation channel for nitromethane following $\pi^* \leftarrow \pi$ (226 nm) excitation. Therefore, we perform similar pump-probe experiments at 271 nm excitation of nitromethane to probe the generation of OH radicals. Under the detection sensitivity limit of our LIF spectrometer for OH species, no OH radical fluorescence signal is observed. This observation is in good agreement with Greenbaltt and co-workers' study,²² in which they did not observe any OH production from photolysis of nitromethane at 282 nm.

Attempts are also made to detect the CH_3 and CH_3O radicals following the 271 nm excitation of nitromethane under collisionless conditions, but no signal for either CH_3 or CH_3O is

CH_3NO_2 271 nm (170 fs)

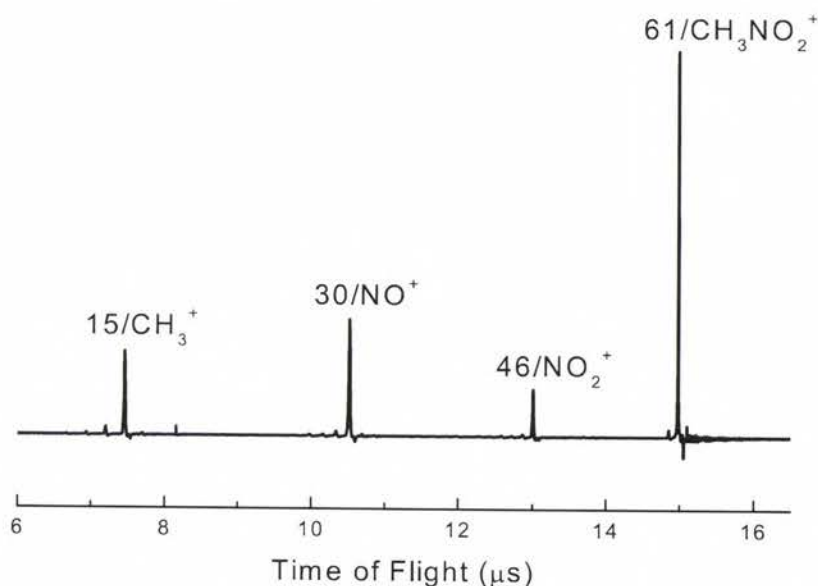


Figure 3.12: Mass spectrum of the photolysis of nitromethane following $\pi^* \leftarrow n$ excitation at femtosecond 271 nm. Intense parent ion signal at mass channel 61 amu is observed.

Figure 3.12 shows the TOFMS of the photolysis of nitromethane at femtosecond 271 nm excitation. Three fragment ions (CH_3 , NO_2 and NO) are observed with only minor intensities, and the nitromethane parent ion is observed with major intensity. The minor fragment ion signal intensity could be explained in two different ways: one is that most of the excited parent molecules are ionized by absorption of another two photons at 271 nm, and only very small portion of the excited molecules dissociates into CH_3 and NO_2 after rupture of C- NO_2 bond. After the dissociation occurs, the fragments can be further ionized by absorption of another three photons at

271 nm. We call this a dissociation-ionization mechanism. In this case, the linewidth for the parent ion mass peak and fragment ion mass peaks should be about the same (10 ns), and no broadening should occur to the fragment ion mass peaks. The other possible mechanism for these TOFMS signals is that all the excited parent molecules are first ionized through resonance enhanced three-photon ionization, then some parent ions further dissociate into fragment ions within hundreds of nanoseconds inside the ionization region of the TOFM spectrometer. We call this an ionization-dissociation mechanism. In this later case, however, the linewidth for the fragment ion mass peaks will be broadened due to the fragmentation of nitromethane parent ion. Since the excess energy in the nitromethane parent ion is about 2 eV ($3 \times 4.57 - 11.08$ (IE) = 2 eV) after absorbing three photons at 271 nm, this is enough excess energy to open the three fragmentation channels to produce CH₃, NO₂ and NO ions directly from the parent ions.⁵² The nitromethane parent ion mass peak has a linewidth of 10 ns, which is comparable to the instrumental linewidth of the TOFMS spectrometer, but the linewidth for the three fragment ion mass peaks in Figure 3.12 varies from 18 to 25 ns, which shows about 10 ns linewidth broadening for these fragment peaks. These broadened linewidths are evidences that the fragment ions are generated from fragmentation of the nitromethane parent ion, rather than from ionization of neutral dissociation products following $\pi^* \leftarrow n$ excitation of nitromethane. Combined with the nanosecond 271 nm pump-probe experiments, for which no NO₂, CH₃, CH₃O, or OH product signals are observed, we suggest that the ionization-dissociation mechanism is more probable for the production of the three fragments with only minor signal intensity. This mechanism is in good agreement with results reported by Kilics *et al.* for

multiphoton ionization and dissociation of nitromethane using 375 nm femtosecond laser pulses.⁵² The ionization-dissociation mechanism means that the nitromethane does not dissociate following $\pi^* \leftarrow n$ excitation at 271 nm in a supersonic molecular beam under collisionless conditions. This conclusion is in good agreement with Kwok *et al.*'s results that no dissociation products are observed after excitation of nitromethane at 266 nm under collision-free conditions.³⁶

In order to confirm the validity of the proposed ionization-dissociation mechanism for the excitation of nitromethane at 271 nm, femtosecond pump-probe experiments are performed to measure the dynamics of the production of the three fragment ions. In this experiment, the pump beam at 271 nm is used to excite the parent molecule, and the probe beam at 406.5 nm is used to ionize the parent and fragments. The laser intensity of both pump and probe beams are kept low enough to reduce the ion signal by a factor of 100 produced by only a single beam. If nitromethane molecule dissociates into CH₃ and NO₂ after the excitation at 271 nm, the pump-probe transients for both CH₃ and NO₂ should present as a buildup near zero delay time, then reach a constant plateau after some longer delay time. On the contrary, if the nitromethane molecule does not dissociate at the ($n\pi^*$) excited electronic state after 271 nm excitation, then we will see an ion signal enhancement for the nitromethane parent mass channel when both pump and probe beams are overlapped around zero delay time. Additionally, the lifetime of the excited state of nitromethane could be extracted from the pump-probe transient employing a single exponential decay function if it is long enough. Moreover, the fragment ion signal should have similar enhancement behavior around zero delay time since the fragment ion signal intensity is proportional to the

parent ion signal intensity. In terms of energy for ionization, after excitation by a single photon at 271 nm, the nitromethane molecule needs another three photons at 406.5 nm to be ionized. The excess energy in the parent ion is about 2.6 eV ($1 \times 4.57 + 3 \times 3.05 - 11.08$ (IE) = 2.64 eV), which is also enough to open the three dissociation channels for the fragments.

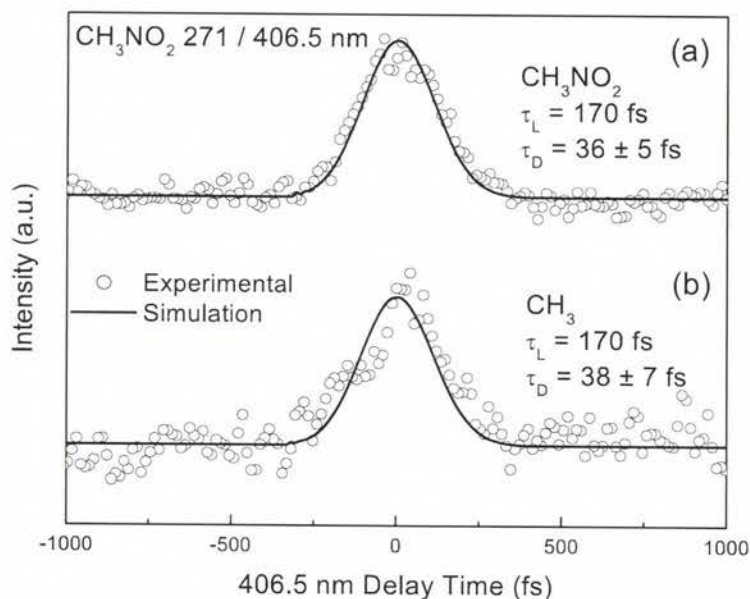


Figure 3.13: Femtosecond pump-probe transients for the nitromethane parent (a) and CH₃ fragments (b) following the excitation of nitromethane at 271 nm. A 406.5 nm laser pulse is used as the probe beam. Open circles are experimental measurements, solid lines are fits with a single exponential decay. Both transients show a fast decay ($\tau_D \approx 36$ fs) in the ($n\pi^*$) excited electronic state of nitromethane. See text for further discussion.

Figure 3.13 displays the pump-probe transients obtained by monitoring the nitromethane parent ion and CH₃ fragment ion mass channel. We do not observe a buildup around the zero delay time for the CH₃ fragment pump-probe transient, nor do we observe a constant plateau after a longer delay time. A signal enhancement when both pump and probe beams are overlapped is observed, however, which is similar to

the pump-probe transient for the nitromethane parent ion. The transients for NO₂ and NO fragments are similar to that for the CH₃ fragment. This result further confirms that the fragment ions are produced from dissociation of the nitromethane parent ion. After deconvolution of the pump-probe transient of nitromethane parent ion from pump-probe pulse cross-correlation ($\tau_L=170$ fs), a single exponential decay with a decay constant (τ_D) of 36 fs is determined. Since the exponential signal decay is induced due to the depletion of the excited ($n\pi^*$) state population of nitromethane, we interpret the decay time constant to be the lifetime of the ($n\pi^*$) state of nitromethane. To the best of our knowledge, this is the first time that the lifetime of the excited ($n\pi^*$) state of nitromethane is determined. The ultra-short lifetime of the ($n\pi^*$) state can well explain the broad absorption spectrum around the $\pi^* \leftarrow n$ transition of nitromethane. The reliability of the pump-probe measurement is confirmed by the duplication of the pump-probe transients for NO and NO₂ ions from the dissociative multiphoton ionization of NO₂ gas at around 400 nm, which has been reported by Eppink *et al.*⁵³ The pump-probe transients for both NO and NO₂ ions obtained in our measurements are comparable to those observed by Eppink and co-works.

3.4 Conclusions

After performing many experiments and careful analysis of the experimental data, we can integrate most of the existing photodissociation mechanisms for nitromethane following its two most intense absorption excitations, $\pi^* \leftarrow \pi$ and $\pi^* \leftarrow n$. Our conclusions based on our own work and that of others are presented below.

Direct observation of intense CH₃, NO₂ (fs) and NO product signals from the photodissociation of nitromethane at 226 and 193 nm excitations confirms that the C-

NO₂ bond rupture is the main primary process for the photolysis of nitromethane following the $\pi^* \leftarrow \pi$ excitation. Observations of OH and CH₃NO species with low quantum yield prove that OH formation and O atom elimination are minor channels for the dissociation of nitromethane after the $\pi^* \leftarrow \pi$ excitation. Formation of CH₃O radical after the dissociation of nitromethane at 226 and 193 nm excitation under only collisional conditions further confirms that the CH₃O radical is a result of the recombination of CH₃ and NO₂ products, and the nitro-nitrite isomerization does not occur for nitromethane following $\pi^* \leftarrow \pi$ excitation. Femtosecond pump-probe experiments at 226 nm show that the dynamics of the formation of CH₃ and NO₂, namely, the photodissociation dynamics of the nitromethane after the $\pi^* \leftarrow \pi$ excitation, is faster than our laser pulse duration (180 fs).

In nanosecond 271 nm laser experiments, a pump-probe scheme is employed to detect NO₂, CH₃, CH₃O and OH products following the dissociation of nitromethane in the ($n\pi^*$) excited electronic state; however, none of these fragments is observed. In femtosecond 271 nm laser experiments, nitromethane parent ion is observed with major intensity, together with three fragment ion signals (CH₃, NO₂ and NO) with only minor intensities. Pump-probe transients for both nitromethane parent and fragment ions at 271 nm excitation display a fast exponential decay with a time constant of 36 fs. We interpret this decay constant to be the lifetime of the excited ($n\pi^*$) state of nitromethane. Combined with the 271 nm nanosecond pump-probe experiments, for which NO₂, CH₃, CH₃O, and OH fragment are not observed, we conclude that all the fragment ions generated in 271 nm femtosecond laser experiments are derived from the parent ion,

and dissociation of nitromethane from the ($n\pi^*$) excited electronic state does not occur in a supersonic molecular beam under collisionless conditions.

3.5 Acknowledgment

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CHAPTER 4

Excited Electronic State Decomposition of Furazan Based Energetic Materials: 3,3'-diamino-4,4'-azoxyfurazan (DAAF) and its Model Systems, Diaminofurazan (DAF) and Furazan

Work Presented in this chapter is published in “Guo, Y. Q.; Bhattacharya, A.; Bernstein, E. R. *J. Chem. Phys.* **2008**, *128*, 034303.” Yuanqing and I worked together on the experiments and I worked independently on the theoretical calculations.

4.1 Introduction

Recently a series of furazan based new energetic materials, especially DAAF (3,3'-diamino-4,4'-azoxyfurazan), have received great attention due to their favorable properties including good heat resistivity, high heat of formation, low sensitivity, and good detonation performance for applications as high explosives, fuels, and propellants.¹ The structure of DAAF (illustrated in Figure 4.1) consists of two aromatic amino furazan rings connected by an azoxy group. As an excellent candidate for an insensitive energetic material, DAAF has acceptable thermal stability and compatibility for solid propellant applications, and can be used as an energetic additive to modify the blast properties of nitramine based composite propellant formulations. In addition,

DAAF is also an attractive additive for rocket propellant and TATB (triamino trinitrobenzene) based explosive formulations. Several studies of the relative thermal stability and detonation performance of DAAF in condensed phase have been performed.²⁻⁴ Differential scanning calorimetry (DSC) and thermogravimetric (TG) analysis of the thermal decomposition of DAAF reveal that it is stable up to 230 °C and that NH₂OH, NH₂CN, NH₃, and HCN are major thermal decomposition products of DAAF.⁵ Based on the decomposition product distribution, a possible pathway for thermal decomposition of DAAF in the condensed phase has been suggested to be simultaneous cleavage of furazan rings and the azoxy group.

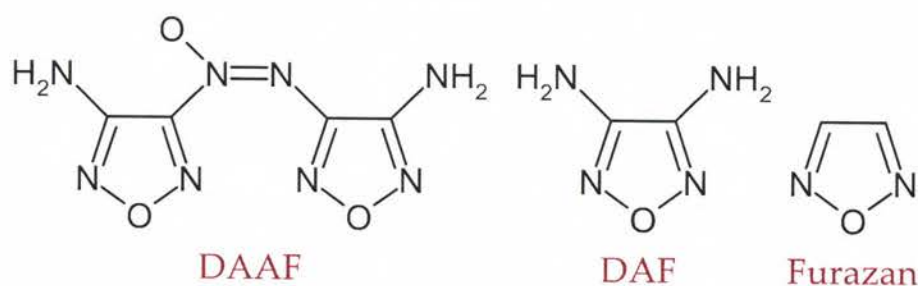


Figure 4.1: Chemical structures of furazan based energetic material (DAAF), model systems (DAF and furazan).

DAF (diaminofurazan, see Figure 4.1), one of the non-energetic model systems for furazan based energetic materials, is used as a precursor in the synthesis of many furazan based, high nitrogen content, insensitive energetic materials, including DAAF. Although DAF does not have the promising energetic features of DAAF, it displays great potential as ballistic modifier in RDX incorporated, double base propellant formulations. DSC and differential thermal analysis reveal that DAF thermally decomposes in condensed phase through a two stage pathway in which kinetics of the initial stage of thermal decomposition of DAF is governed by an activation energy of

67 kJ/mol. Gaseous species, such as CN, NH, OH, and oxides of nitrogen have been identified as thermal decomposition products of DAF through TG-FTIR analysis.⁶ The suggested mechanism for the initial thermal decomposition of DAF in condensed phase is rupture of the C-NO bond. For the furazan molecule, which forms the backbone of DAAF and DAF, both gas phase thermal decomposition and photolysis in ether solution reveal that the cleavage of two ring-bonds (C-C and N-O) followed by subsequent rearrangement of the ring yields hydrogen cyanide (HCN) and hydrogen isocyanate (HNCO) as products.^{7,8}

Although the aforementioned studies of thermal decomposition of DAAF and DAF in condensed phase have exposed thermal stability and thermal decomposition mechanisms for these materials, little information about the difference between intramolecular and intermolecular behavior, as well as the fundamental decomposition properties of the individual molecules, can be extracted. Additionally, ignition processes involving sparks, shock, slow/rapid heating, lasers, and arcs can all initiate the decomposition reaction of energetic material by generating excited electronic states. Decomposition of energetic materials from excited electronic states has been experimentally proved to play an important role in their overall decomposition mechanisms and kinetics.⁹⁻¹⁴ Thus, investigations of isolated, gas phase molecular decomposition of DAAF and model systems (DAF and furazan) in excited electronic states will yield an improved understanding of initial excited electronic state decomposition mechanisms and dynamics of furazan based energetic materials at a fundamental level. To the best of our knowledge, no investigation of the gas phase

unimolecular decomposition of furazan based energetic materials and model systems has been reported in literature to date.

This chapter addresses the first systematic experimental and theoretical study of the excited electronic state decomposition of these materials. DAF and furazan are selected as model systems because DAAF and these two molecules have similar delocalized aromatic five-membered heterocyclic rings that have spectroscopically active low lying (π, π^*) excited electronic states. On the other hand, DAF and furazan are non-energetic materials. Therefore, a systematic comparison of the excited electronic state decomposition mechanism for DAAF and its model systems (DAF and furazan) will generate more insight into and understanding of the initial decomposition mechanisms and dynamics of furazan based energetic materials.

Both nanosecond (ns) energy resolved and femtosecond (fs) time resolved spectroscopies have been employed to investigate the excited electronic state decomposition mechanisms and dynamics of isolated gas phase furazan based molecules (DAAF, DAF, furazan). These three molecules are excited to their (π, π^*) excited electronic state by absorption of a single UV photon and a dissociation product, nitric oxide (NO) is observed by a one-color (1+1) resonance enhanced two-photon ionization (R2PI) scheme using time of flight mass spectrometry (TOFMS) detection. Three vibronic transitions [$A^2\Sigma (v'=0) \leftarrow X^2\Pi (v''=0,1,2)$] of the NO molecule from both DAAF and DAF are observed; only two vibronic bands of the NO product from furazan are observed. The NO product from DAAF is generated through an excitation wavelength independent nonadiabatic dissociation channel, and characterized by a rotationally cold (20 K) and vibrationally hot (1260 K) internal energy distribution. The

rotational and vibrational distributions of the NO product from DAF and furazan are dependent on the excitation wavelengths. Complete active space self consistent field (CASSCF) calculations are pursued on furazan and DAF to generate more detailed energetics of their excited electronic state decomposition pathways. These calculations reveal that DAF and furazan comes back to an (n,π^*) state following initial electronic excitation to (π,π^*) state through $(S_2/S_1)_{CI}$ and an energy barrier for the $(S_1/S_0)_{CI}$ conical intersections between the (n,π^*) excited electronic state and ground electronic state plays an important role in the excited electronic state decomposition pathways of these molecules. DAF and furazan possess two different pathways of decomposition: ring contraction and ring opening. These two pathways are electronically nonadiabatic. The ring contraction mechanism generates rotationally cold (20 K) product NO and the ring opening mechanism generates rotationally hot (100 K) product NO. Furazan based energetic material (DAAF) however, dissociates only through a ring contraction mechanism. Femtosecond pump-probe experiments at 226 nm show that the formation dynamics of the NO product from DAAF falls into the time scale of our laser pulse duration (180 fs). Two additional fragments with mass of 40 amu ($C_2H_2N^+$) and 28 amu (CH_2N^+) are observed in mass spectrum of furazan for 226 nm (1+1) femtosecond ionization. NH_2 is not observed as a secondary decomposition product of DAAF and DAF within our detection limit.

4.2 Experimental Procedures

Detailed experimental procedures for both nanosecond (ns) laser energy resolved and femtosecond (fs) laser pump-probe spectroscopy have been described elsewhere.¹⁵⁻¹⁸ Briefly, the experimental setup consists of laser systems with both ns

and fs time duration, a supersonic jet expansion nozzle with a laser desorption attachment, and two vacuum chambers: a time of flight mass spectrometer chamber and a laser induced fluorescence (LIF) chamber. For the ns laser experiments, a single pump-probe laser beam at three wavelengths (226 nm, 236 nm and 248 nm) is used both to initiate dissociation of furazan based molecules and detect NO following a one color (1+1) R2PI scheme [$A^2\Sigma (v'=0) \leftarrow X^2\Pi (v''=0,1,2)$ and $I \leftarrow A$ transitions] through TOFMS. The three UV laser wavelengths used in the ns laser experiments are generated by a pulsed dye laser, pumped by the second harmonic (532 nm) of a Nd:YAG laser's fundamental output (1.064 μm), in conjunction with a nonlinear wavelength extension system. Typical pulse energy of the UV laser is 200-600 $\mu\text{J/pulse}$ depending on the exact wavelength of interest for a one-color experiment, which gives a laser beam intensity (I) ~ 1.3 to $4 \times 10^7 \text{ W/cm}^2$ for an 8 ns pulse duration at a focused beam diameter of 0.5 mm. For detection of an NH_2 product from DAF and DAAF through TOFMS, a UV laser beam at 226 nm is used to initiate the dissociation of the parent molecules and two additional laser beams are required to excite and ionize the NH_2 product: one at 600 nm and another at 118 nm corresponding to $A^2A_1(0,9,0) \leftarrow X^2B_1(0,0,0)$ and $I \leftarrow A$ transitions, respectively. For the detection of the NH_2 product through LIF only one additional laser beam (569 nm) is required to excite NH_2 $A^2A_1(0,10,0) \leftarrow X^2B_1(0,0,0)$ transition. Detection of the NH_2 product from DAF and DAAF has been calibrated by the observation of the NH_2 radical generated by photolysis of ammonia (NH_3) at 193 nm inside a quartz capillary attached to the pulse nozzle.

For fs pump-probe experiments, a single laser beam at 226 nm is equally split into pump and probe beams. The sample molecules are excited by the pump beam and dissociate according to their dissociation dynamics. Dissociation products are subsequently ionized by the time delayed probe beam and detected via TOFMS. By delaying the probe beam with respect to the pump beam, product appearance times can be determined. The fs laser light is generated by a femtosecond laser system consisting of a self-mode-locked Ti:Sapphire oscillator (KM Labs), a home-made ring cavity Ti:Sapphire amplifier, and a commercial traveling optical parametric amplifier of super fluorescence (TOPAS, Light Conversion) system. Pulse duration of the deep UV laser pulse is measured to be 180 fs using a self-diffraction (SD) autocorrelator and off-resonance two-photon absorption of the furan molecule.¹⁹ Typical pulse energy of the deep UV output is $\sim 1 \mu\text{J/pulse}$. For one-color time resolved investigations, the energy of pump and probe pulses are kept at an optimum value of $\sim 200 \text{ nJ/pulse}$ ($I \sim 5.66 \times 10^8 \text{ W/cm}^2$) to improve signal-to-noise ratio and to avoid uncontrolled fragmentation due to multiphoton absorption by the parent molecule.

The isolated gas phase DAAF and DAF molecules are produced through a combination of matrix assisted laser desorption (MALD) and supersonic jet expansion. The nozzle employed for the sample beam generation is constructed from a Jordan Co. pulsed valve and a laser desorption attachment.^{20,21} Sample drums for matrix desorption are prepared by wrapping a piece of porous filter paper around a clean aluminum drum. A solution of equimolar amounts of sample and matrix (R6G dye) in acetone is uniformly sprayed on the sample drum. An air atomizing spray nozzle (Spraying System Co.) with siphon pressure of 10 psig is used to deposit the DAAF/DAF and

R6G on the drum surface. During the spraying, the drum is rotated and heated with a halogen lamp to make sure that the coating is homogeneous and dry. The dried sample drum is then placed in the laser ablation head/nozzle assembly and put into a vacuum chamber. In order to maintain fresh sample area for each laser ablation shot, a single motor is used to rotate and translate the sample drum simultaneously. DAAF/DAF molecules are desorbed from the drum by laser ablation at 532 nm, entrained in the flow of helium carrier gas through a 2 by 60 mm channel in the ablation head, and expanded into the vacuum chamber.^{22, 23} Since furazan is liquid with a high vapor pressure (170 Torr at 25^o C), a 1% furazan-He gas mixture is prepared by premixing He carrier gas with the vapor of a liquid furazan sample and directly expanded it into the vacuum system to form a molecular beam.

The experiment is run at a repetition rate of 10 Hz. The timing sequence for the pulsed nozzle, ablation laser, and ionization laser is controlled by a time delay generator (SRS DG535). The molecular beam is perpendicularly crossed by a UV laser beam that is focused to a spot size of about 0.5 mm at the ionization region of a time of flight mass spectrometer. A background pressure of 1×10^{-5} Torr is maintained in the vacuum chamber during the experiment. Ion signals are detected by a microchannel plate detector (MCP). Signals are recorded and processed on a personal computer using a box car averager (SRS SR 250) and an analogue-to-digital conversion (ADC) card (Analog Devices RTI-800). For time resolved experiments, the delay time between the pump and probe beam is controlled by a microtranslation stage (Thorlabs: LNR50SEK1) with a step size of 13 fs. Each point on the pump-probe transient spectrum corresponds to an average intensity resulting from 100 laser shots.

Commercial furazan and DAF (Labotest) are used without any additional purification. DAAF is supplied by Los Alamos National Laboratory (M. Hiskey) and is used without any further purification.

4.3 Computational Procedures

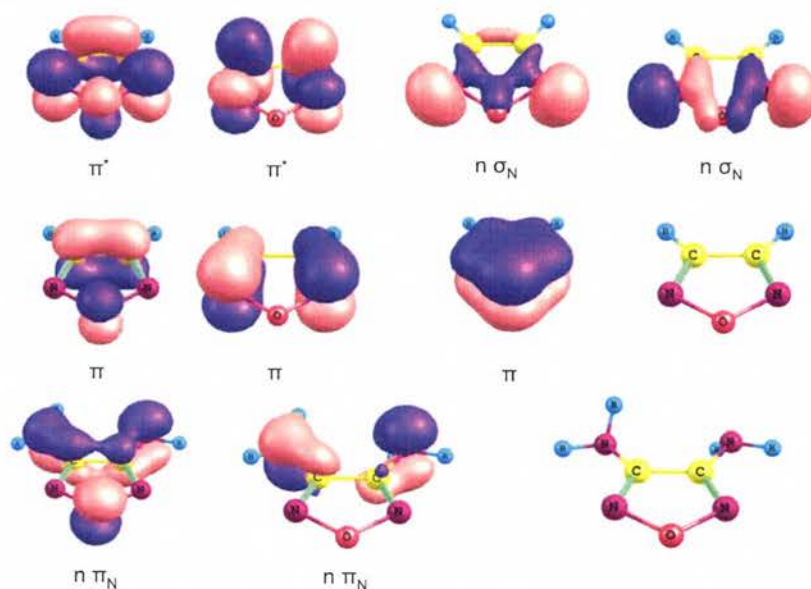


Figure 4.2: Orbitals used in the active space of CASSCF calculations for furazan and DAF. Three bonding π orbitals, two anti-bonding π^* orbitals, and two in-plane N non-bonding $n\sigma_N$ orbitals are included in the active space for furazan. In addition, two more nonbonding $n\pi_N$ of the amino groups of DAF are included in the active space for DAF.

Potential energy surface calculations and geometry optimizations for furazan and DAF are executed at the CASSCF/6-31G* level of theory with Gaussian03 program.²⁴ No symmetry restrictions are applied during the calculations. For the excited state potential energy surface calculations, the minimum active space comprises 10 electrons in 7 orbitals, denoted as CASSCF(10,7) for furazan and 14 electrons in 9 orbitals, denoted as CASSCF(14,9) for DAF. Orbitals used in the active space are three bonding π , two antibonding π^* , and two in-plane N nonbonding $n\sigma_N$ for furazan. In

addition to these orbitals, two more nonbonding $n\pi_N$ of the amino groups of DAF, which can take part in the π delocalization of the ring, are included in the active space of DAF. The active orbitals are shown in Figure 4.2. The 2s nonbonding orbital of the O atom is excluded from the active space because it is lower in energy than the above orbitals and does not take part in the excitation.

Vertical excitation energies are computed by state-averaging over the ground state and two successive singlet excited states with equal weights. For reliable estimation of vertical excitation energies, MP2 correlated CASSCF energies are also calculated with the active spaces (10,7) and (14,9) for furazan and DAF, respectively. As the S_1 excited electronic surface for both furazan and DAF is an (n,π^*) excited state, the active space for the optimization of the critical points (local minimum and conical intersections) on the S_1 surface should include all the bonding and antibonding π orbitals and two in-plane N nonbonding $n\sigma_N$ orbitals. The geometries of the critical points are optimized with state averaging over S_0 and S_1 states with equal weights. Thus, the S_1 minimum denoted as $(n,\pi^*)_{\text{Min}}$ and two conical intersections between the S_1 surface and the S_0 ground electronic surfaces in two different reaction coordinates, denoted as $(S_1/S_0)_{\text{CI,a}}$ and $(S_1/S_0)_{\text{CI,s}}$ are optimized with active spaces (10,7) and (14,9) for furazan and DAF, respectively. The conical intersection between S_2 and S_1 excited electronic surfaces, denoted as $(S_2/S_1)_{\text{CI}}$ is also optimized with the same active space. As the S_2 excited electronic surface for both furazan and DAF is a (π,π^*) excited state, the active space for the optimization of the critical points (local minimum) on the S_2 surface should include all the bonding and antibonding π orbitals. Transition state (TS)

structures on the S_0 ground electronic surface are characterized by analytical frequency calculations.

4.4 Experimental Results

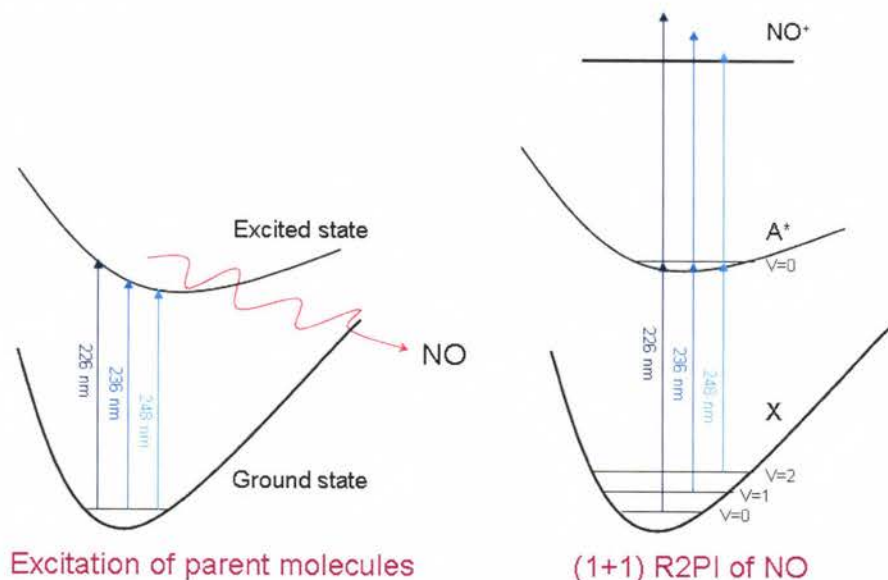


Figure 4.3: Excitation processes and detection schemes. The parent molecule is excited and fragmented by absorption of single UV photon at three excitation wavelengths, and the product (NO molecule) is probed through one-color (1+1) R2PI technique through three vibronic transitions [$A^2\Sigma (v'=0) \leftarrow X^2\Pi (v''=0,1,2)$] of the NO molecule.

A detection scheme diagram for the investigation of the excited electronic state decomposition of furazan based energetic materials and the model systems is shown in the Figure 4.3. The parent molecule of interest is excited to an excited electronic state by absorption of a single UV photon of three excitation wavelengths (226 nm, 236 nm and 248 nm). The parent molecules decompose into products through certain decomposition pathways. In ns laser experiments, nitric oxide (NO) is observed as a major initial dissociation product in the excited electronic state decomposition of DAAF, DAF and furazan. The NO product is probed using a one-color (1+1) R2PI detection scheme through TOFMS. The three excitation wavelengths used in this work

also correspond to the resonance absorption of (0-0), (0-1) and (0-2) vibronic bands of the $A^2\Sigma \leftarrow X^2\Pi$ electronic transitions of the NO product, respectively. By scanning the ns laser excitation wavelength, a (1+1) R2PI rotationally resolved spectrum of the NO product from different parent molecules is recorded.

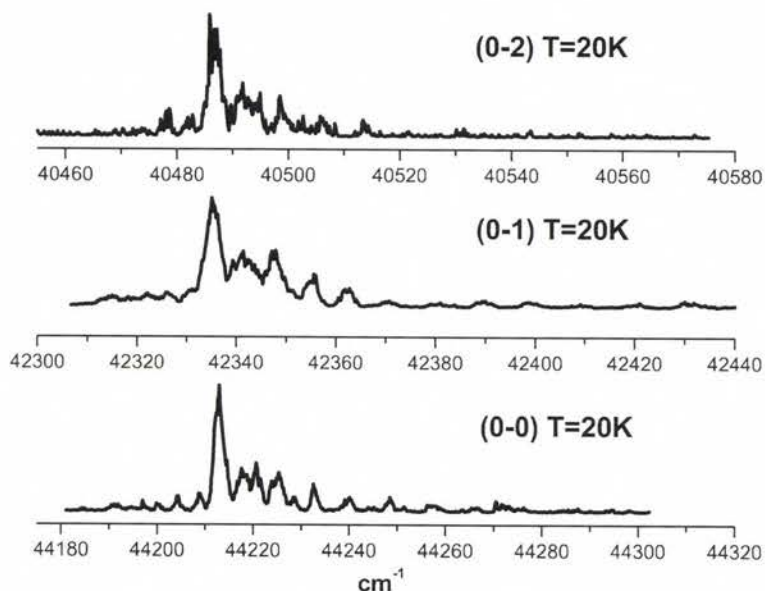


Figure 4.4: One-color (1+1) R2PI spectra of the vibronic transitions [$A^2\Sigma^+ (v'=0) \leftarrow X^2\Pi (v''=0,1,2)$] of the NO product from the excited electronic state decomposition of DAAF molecule. Rotational temperature simulations with Boltzmann distribution show that the three observed vibrational levels on the ground electronic states have a similar rotational temperature of 20 K.

(1+1) R2PI spectrum of the three vibronic transitions, $A^2\Sigma^+(v'=0) \leftarrow X^2\Pi(v''=0,1,2)$ of the NO molecule observed from decomposition of DAAF from its excited electronic state are shown in Figure 4.4. The three spectra in this figure have similar rotational structure but have a different absolute intensity for each vibronic band. The most intense feature in each spectrum of NO from DAAF can be assigned as the ($Q_{11} + P_{12}$) band head of each vibronic band, and the less intense features within each spectrum are due to other rovibronic transitions.^{25,26} Spectral

simulation based on the Boltzmann population distributions for the three vibronic transitions of the NO product from DAAF produces similar rotational temperatures ($\sim 20\text{K}$) for three vibrational levels ($v''=0,1,2$) in the ground electronic state. The vibrational temperature of the NO product from DAAF can also be obtained by simulating the relative intensities among the observed vibronic bands using Boltzmann population distribution analysis. By comparing the experimental data with simulation at different vibrational temperatures, the vibrational temperature of the NO product from DAAF is estimated to be 1260 K.

Although the matrix assisted laser desorption technique is a good method to place easily fragmented, fragile molecules in the gas phase without fragmentation, great efforts are taken in our previous and present work to ensure that the sample molecules are not fragmented in the ablation process.¹⁵⁻¹⁸ Three different methods have been employed to explore this issue: comparison of NO velocity distributions from the nozzle; determination of arrival time for the NO signal intensity as a function of nozzle/pump laser timing; and NO rotational and vibrational temperature determinations as a function of source of NO. These methods demonstrate that NO from DAAF is generated at the ionization region of the TOFMS, not in the laser desorption region of the nozzle.

Similar (1+1) R2PI spectra of three vibronic transitions, $A^2\Sigma^+(v'=0) \leftarrow X^2\Pi(v''=0,1,2)$ of the NO molecule obtained from excited electronic state decomposition of DAF are shown in Figure 4.5. The (0-0), and (0-1) vibronic bands of the NO product from DAF show similar rotational patterns to those of the NO product from DAAF, and the rotational temperature of these two bands is also about 20 K. The

(0-2) vibronic band of the NO product from DAF shows much hotter rotational distribution than that of the (0-0) and (0-1) vibronic bands. Spectral simulation to the (0-2) band yields a rotational temperature of about 100 K.

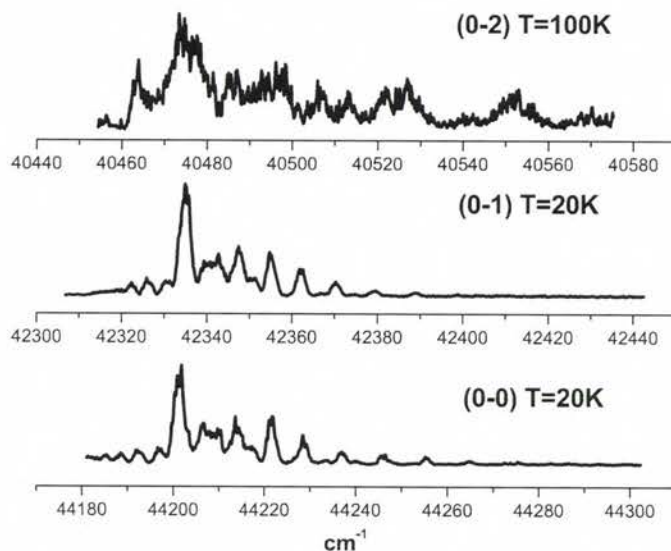


Figure 4.5: One-color (1+1) R2PI spectra of the vibronic transitions [$A^2\Sigma^+$ ($v'=0$) $\leftarrow$ $X^2\Pi$ ($v''=0,1,2$)] of the NO product from the excited electronic state decomposition of DAF molecule. Rotational temperature simulations with Boltzmann distribution show that the $v''=0$ and 1 vibrational levels on the ground electronic state have a similar rotational temperature of 20 K, and the $v''=2$ vibrational level has a rotational temperature of 100 K.

Excited electronic state decomposition of the furazan molecule generates NO products with only $v''=0$ and 1 population, and the spectra of the two observed vibronic bands, (0-0) and (0-1), of the NO product are illustrated in Figure 4.6. The spectral structure of the (0-0) band of the NO product from furazan is similar to that of the NO product from both DAAF and DAF; however, the (0-1) vibronic band shows a hot rotational pattern with a temperature of about 130 K. No (0-3) spectrum of NO from DAF and (0-2) spectrum of NO from furazan are obtained.

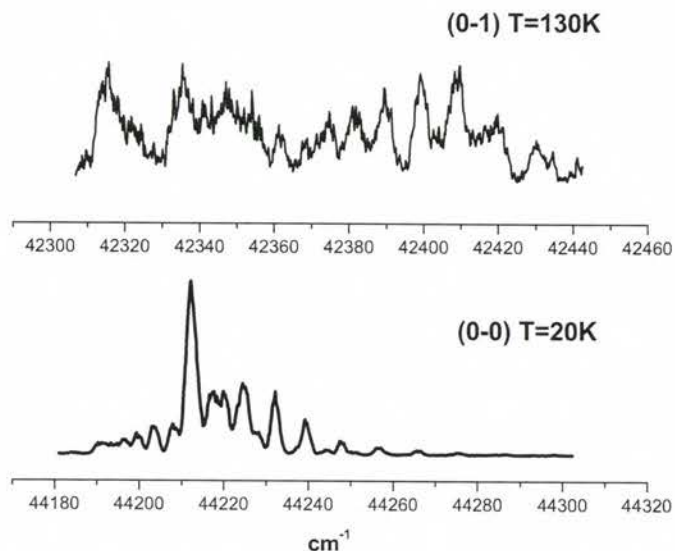


Figure 4.6: One-color (1+1) R2PI spectra of the vibronic transitions [$A^2\Sigma^+$ ($v'=0$) $\leftarrow$ $X^2\Pi$ ($v''=0,1$)] of the NO product from the excited electronic state decomposition of furazan molecule. Rotational temperature simulations with Boltzmann distribution show that the $v''=0$ vibrational level on the ground electronic states have a rotational temperature of 20 K, and the $v''=1$ vibrational level has a rotational temperature of 130 K.

Therefore, only NO product is observed in ns laser experiments as the major initial product in the excited electronic state decomposition of DAAF, DAF and furazan. Table 4.1 gives rotational temperatures for each populated vibrational level of the NO product from both energetic material and model systems.

The NO product from DAAF displays similar cold rotational distributions (20 K) at all three excitation wavelengths (226 nm, 236 nm and 248 nm): this implies that excited electronic state decomposition of DAAF follows a single, excitation wavelength independent, dissociation channel. The model systems, on the other hand, show excitation wavelength dependent dissociation channels. For example, dissociation of furazan at 236 nm and DAF at 248 nm renders hot rotational distributions for the NO product, whereas excitation of furazan at 226 nm and DAF at 226 and 236 nm yields

cold rotational distributions for the NO fragmentation product. This difference in mechanistic behavior can be rationalized by the fact that DAAF must have dissociative excited states which can provide a barrierless single decay channel for excited state decomposition of this material. For the model systems, on the other hand, there is some barrier in the excited state decomposition pathway which can alter the decomposition channel from the excited electronic state. More detailed exploration of these different evolution pathways from the excited electronic state with respect to relevant reaction coordinates will be presented in the Discussion Section below.

Table 4.1: Rotational temperatures for the $[A^2\Sigma(v'=0) \leftarrow X^2\Pi(v''=0,1,2)]$ transitions of the NO product from ns laser excited electronic state decomposition of energetic material, DAAF and its model systems, furazan and DAF.

Compounds	Rotational Temp. A $\leftarrow$ X (0-0)	Rotational Temp. A $\leftarrow$ X (0-1)	Rotational Temp. A $\leftarrow$ X (0-2)
DAAF	20 K	20 K	20 K
Furazan	20 K	130 K	
DAF	20 K	20 K	100 K

The NH₂ radical generated by photolysis of NH₃ at 193 nm excitation is detected by both TOFMS and LIF. These detection schemes and rotationally resolved two color (1+1') R2PI spectrum of NH₂ obtained from photolysis of NH₃ serve as standard calibration of the apparatus for the detection of the NH₂ product from DAF and DAAF. No NH₂ product is observed by either TOFMS or LIF detection from decomposition of DAF or DAAF, which eliminates the possibility of the NH₂ as

secondary decomposition product (or intermediate precursor) for the excited electronic state decomposition of these two molecules.

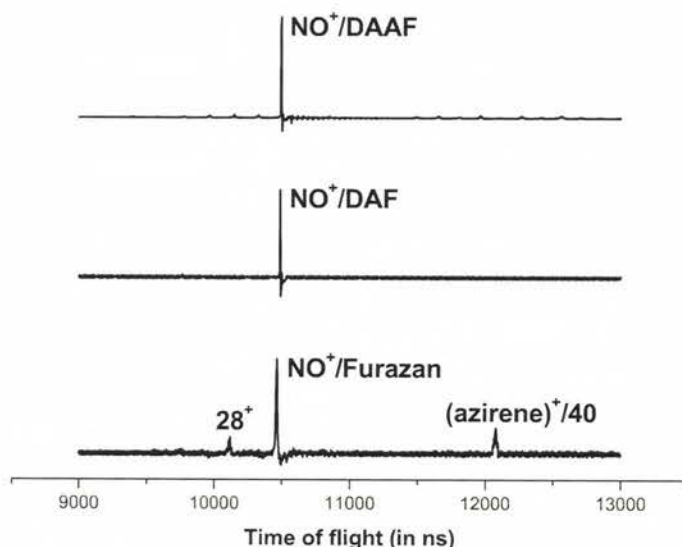


Figure 4.7: Mass Spectra of the excited electronic state decomposition of DAAF, DAF and furazan using fs laser pulse at 226 nm. The time duration of the fs laser pulse is about 180 fs. The NO molecule is the only observed product from DAAF and DAF; two additional mass channels (28 and 40 amu) are observed from furazan.

The time of flight mass spectra of DAAF, DAF and furazan obtained by the resonance excitation with 180 fs laser pulses at 226 nm are shown in Figure 4.7. The NO molecule corresponding to mass channel 30 amu is still the only observed decomposition product from both DAAF and DAF in the fs time regime. No parent ion is observed for any of these three molecules. For the furazan molecule, besides the NO mass channel, two additional mass channels corresponding to 40 amu and 28 amu are observed. These two mass channels can be assigned as aziriny cation ($C_2H_2N^+$) and methylene amidogenyl cation (H_2CN^+), respectively. The aziriny cation consists of three-membered ring with aromatic properties, and is the most stable species among the possible $C_2H_2N^+$ isomers.²⁷ Methylene amidogenyl cation has also been observed from

two color ns pump-probe experiment of excited electronic state decomposition of furazan at 226 nm (pump) excitation and products are probed by 193 nm. According to the fragments observed due to the excited electronic state decomposition of furazan, both in the ns and the fs time regimes, a five-membered heterocyclic furazan ring rupture mechanism with dissociation of a CN and an NO bond can be proposed for the initial decomposition of furazan.

Figure 4.8 displays fs pump-probe transients for the NO product from DAAF (b) as well as NO molecule from NO gas (a) at 226 nm. As mentioned above, the NO molecule has a resonant single photon absorption for the $A^2\Sigma (v'=0) \leftarrow X^2\Pi (v''=0)$ transition at 226 nm. Both pump and probe beams have the same wavelength. As described in our previous report¹⁷, the gas phase DAAF molecule is pumped to its first excited electronic state by the pump beam, then dissociates into products which are probed by the delayed probe beam. The dynamics of the decomposition are measured via the NO molecule appearance. If decomposition of DAAF is slower than the time duration of pump and probe beams (180 fs), an (exponential) onset of the NO ion signal will be observed as the relative delay time between pump and probe beams is scanned. If decomposition of the energetic materials is much faster than the pulse duration, NO product will be excited by the pump beam in addition to the probe beam, and the lifetime of the NO excited state, which is several hundred ns, will be detected by the probe beam, and the pump-probe transient for the NO product should be a flat horizontal line within a many ps time interval. The transients in Fig. 4.8 show a roughly steady NO ion signal from DAAF, which is the same as NO gas, indicating the

decomposition dynamics of DAAF occurs on a faster time scale than the time duration of our laser pulse.

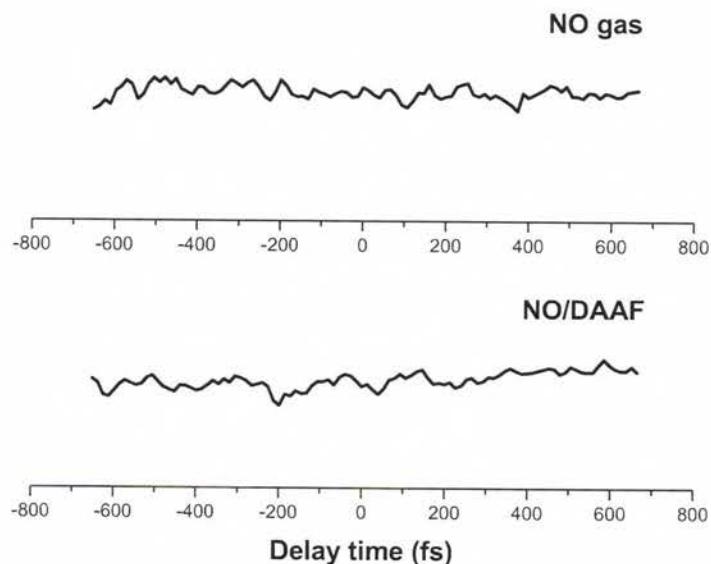


Figure 4.8: One-color pump-probe transients of the NO product from NO gas and DAAF using femtosecond laser pulse at 226 nm. The NO molecule has a resonance absorption at 226 nm due to $[A^2\Sigma^+(v=0) \leftarrow X^2\Pi(v=0)]$ transition.

4.5 Theoretical Results

In order to understand the mechanisms of the excited electronic state decomposition of furazan based energetic materials better, theoretical calculations using the CASSCF method have been performed on the two model systems, furazan and DAF. The vertical excitation energies (E_{vert}) for furazan and DAF, calculated at their CASSCF optimized Franck-Condon (FC) geometries (ground state minimum) of C_1 symmetry are listed in Table 4.2.

Table 4.2: Vertical Excitation energies E_{vert} and state characterization at FC geometry of Furazan and DAF.

Compounds	State	E_{vert} [eV]	
		CASSCF	CAS-MP2
Furazan	$S_1/(n,\pi^*)$	6.09	4.70
	$S_2/(\pi,\pi^*)$	6.55	5.55(5.39 [‡])
DAF	$S_1/(n,\pi^*)$	6.69	4.46
	$S_2/(\pi,\pi^*)$	7.03	4.90

[‡] experimental absorption maximum at 25⁰C in gas phase.²⁸

The E_{vert} at the CASSCF level of theory with 6-31G* basis set is calculated for comparison with relative energies of the critical points on the excited potential energy surfaces. The E_{vert} at the MP2 correlated CASSCF level of theory with the same basis set is calculated with higher accuracy for comparison with experimental excitation energies. Both CASSCF and MP2 correlated CASSCF calculations show that the two lowest-lying excited states for both furazan and DAF are (n,π^*) and (π,π^*) states, which correspond to their S_1 and S_2 excited electronic states, respectively. Moreover, calculated vertical excitation energy of the S_2 (π,π^*) state of furazan with higher accuracy is about 5.55 eV (see Table 4.2), which is in good agreement with the experimental value of 5.39 eV.²⁸ Comparing the three excitation energies (5.49 eV at 226 nm, 5.25 eV at 236 nm and 5.00 eV at 248 nm) used in this work with the calculated vertical excitation energies (5.55 eV and 4.7 eV, Table 4.2) of the S_2 (π,π^*) and S_1 (n,π^*) excited states of furazan molecule, one finds that the furazan molecule is excited to its S_2 (π,π^*) excited state by these three excitation wavelengths. In particular, 226 nm excitation corresponds to the absorption maximum (vertical excitation) for the S_2 (π,π^*) excited state of furazan.

The relative CASSCF energies of the critical points (minimum, conical intersections, transition state) on both excited and ground potential energy surfaces of furazan and DAF with respect to the energy of ground state FC geometry are listed in Table 4.3.

Table 4.3: Relative CASSCF Energies (E_{rel}) of Critical Points, with Respect to Ground-State FC Energy for Furazan and DAF.

Compounds	Structure	E_{rel} [eV]
Furazan	$(S_1/S_0)_{CI,b}$	2.30
	$(S_1/S_0)_{CI,a}$	6.69
	TS_a/S_0	6.29
DAF	$(S_1/S_0)_{CI,b}$	3.05
	$(S_1/S_0)_{CI,a}$	6.04
	TS_a/S_0	5.60

The relative energies of conical intersections $(S_2/S_0)_{CI,a}$, $(S_1/S_0)_{CI,b}$ and transition structure TS_a/S_0 of furazan are 6.69 eV, 2.30 eV, and 6.29 eV, respectively. The relative energies of similar counterparts of DAF are 6.04 eV, 3.05 eV, and 5.6 eV respectively. A schematic one dimensional projection of multidimensional potential energy surfaces of furazan and DAF with locations and structures of different critical points are plotted in Figures 4.9A and B, respectively. Surfaces are computed at CASSCF/6-31G* level of theory and the critical points on the surfaces are computed at CASMP2//CASSCF/6-31G* level of theory. Dotted arrows in these two figures indicate two different possible nonadiabatic pathways: (a) ring contraction through the $(S_1/S_0)_{CI,a}$ conical intersection and (b) ring opening through the $(S_1/S_0)_{CI,b}$ conical intersection.

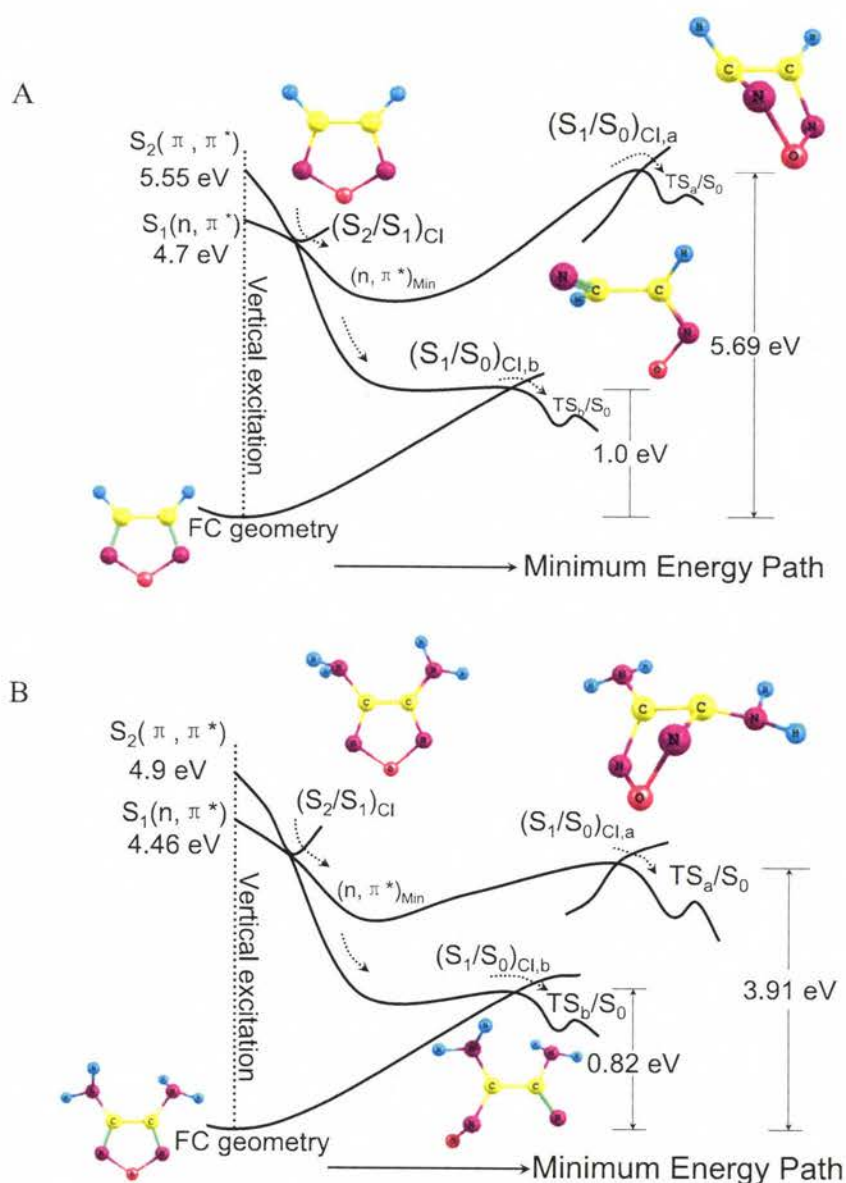


Figure 4.9: One dimensional projection of multidimensional potential energy surfaces of furazan (A) and DAF (B) computed at CASSCF/6-31G* level of theory. Energies of the critical points and conical intersections are computed at CASMP2//CASSCF/6-31G* level of theory. An $(S_1/S_0)_{\text{Cl},a}$ conical intersection is involved in the ring contraction pathway, which can lead the generation of rotationally cold NO initial product. Another $(S_1/S_0)_{\text{Cl},b}$ conical intersection is involved in ring opening pathway, which can finally yield a rotationally hot distribution for the NO product. Note that two nonadiabatic dissociation channels are along two different nuclear co-ordinates.

The optimized ground state geometry (FC geometry) has a planar 5-membered ring for furazan and the additional amine substituents in DAF are pyramidalized. The structure of furazan at the $(S_1/S_0)_{CI,a}$ conical intersection (see Figure 4.9 A) is a ring contracted form (bent and out-of-plane) and is found to have similar energy to that of absorption maximum of the spectroscopically active $S_2 (\pi,\pi^*)$ state. The calculated transition state (TS_a/S_0) structure on the ground electronic surface of furazan, following the $(S_1/S_0)_{CI,a}$ conical intersection shows a similar geometry to that of $(S_1/S_0)_{CI,a}$. The unstable vibrational mode associated with this TS_a/S_0 is found to be a NO-azirene(C_2H_2N) symmetric stretch which indicates the formation of azirene along with NO elimination on the product side. This unstable vibrational mode does not generate any resultant torque acting on the NO moiety. The $(S_1/S_0)_{CI,a}$ conical intersection of DAF has similar structure to that of furazan and is found to be ~ 1 eV in energy lower than that of absorption maximum for the $S_2 (\pi,\pi^*)$ state of DAF. So the computational results suggest that due to vertical excitation to the $S_2 (\pi,\pi^*)$ state, a nonadiabatic dissociation pathway through ring contraction mechanism is possible for these two compounds from FC point of the $S_2 (\pi,\pi^*)$ state though the $(S_1/S_0)_{CI,a}$ conical intersection after crossing the $(S_2/S_1)_{CI}$ conical intersection. This suggested ring contraction decomposition pathway for both molecules would generate NO products with cold rotational distributions because related transition states on their ground electronic surfaces do not generate a large resultant torque on the NO moiety.

The $(S_1/S_0)_{CI,b}$ for both furazan and DAF has an out-of-plane open ring geometry (see Figure 4.9 A and B). For furazan, the $(S_1/S_0)_{CI,b}$ conical intersection is found to be ~ 4.69 eV below its $(S_1/S_0)_{CI,a}$ conical intersection and DAF is found to

have an $(S_1/S_0)_{CI,b}$ conical intersection ~ 3.1 eV below its $(S_1/S_0)_{CI,a}$ conical intersection. For both compounds, the $(S_1/S_0)_{CI,b}$ conical intersection is followed by a transition state (TS_b/S_0) on their ground electronic surface (S_0). This TS_b/S_0 has an unstable torsional mode that clearly indicates a torque acting on NO moiety for NO elimination pathway. Thereby, nonadiabatic dissociation of these two compounds from the FC point (absorption maximum) of the $S_2 (\pi,\pi^*)$ state through their $(S_1/S_0)_{CI,b}$ conical intersection after crossing $(S_2/S_1)_{CI}$ conical intersection can provide hot rotational distributions for the NO product.

Based on the computational results, two different nonadiabatic, radiationless dissociation pathways are possible for the decomposition mechanism of furazan and DAF from their $S_2 (\pi,\pi^*)$ excited electronic state: ring contraction and ring opening. Ring contraction mechanism involves an almost barrierless non-adiabatic dissociation path from the FC point of the $S_2 (\pi,\pi^*)$ state through the $(S_1/S_0)_{CI,a}$ conical intersection after crossing the $(S_2/S_1)_{CI}$ conical intersection when the excitation energy is enough to surmount the $(S_1/S_0)_{CI,a}$ conical intersection. The ring opening mechanism involves an alternate nonadiabatic dissociation path from FC point of $S_2 (\pi,\pi^*)$ state through $(S_1/S_0)_{CI,b}$ conical intersection after crossing $(S_2/S_1)_{CI}$ conical intersection. In the first dissociation mechanism for both furazan and DAF electronic energy can rapidly be thermalised through the $(S_1/S_0)_{CI,a}$ conical intersection by populating out-of-plane vibronically active ring modes following vertical electronic excitation to the $S_2 (\pi,\pi^*)$ state. This pathway must go via an adiabatic state switch from the spectroscopic (π,π^*) to the (n,π^*) state, crossing the $(S_2/S_1)_{CI}$ conical intersection. This process can generate cold rotational distributions of the NO product as the unstable normal mode of vibration

associated with respective transition state (TS_a/S_0) on their ground electronic surface do not possess any resultant torque acting on the NO moiety.

The second alternate channel, on the other hand, can generate hot rotational distributions of the NO product as the unstable normal mode of vibration associated with the related transition state (TS_b/S_0) on the ground electronic surface has a torque acting on the NO moiety for the NO elimination pathway. If electronic excitation of these molecules does not provide sufficient energy to surmount the $(S_1/S_0)_{CI,a}$ conical intersection, electronic energy will eventually be thermalized by populating vibronically active ring opening mode which can lead the deactivation along the $(S_1/S_0)_{CI,b}$ conical intersection, yielding a rotationally hot distribution for the NO product. A similar computation on DAAF, the energetic material, could not be performed at the CASSCF or MP2 correlated CASSCF level of theory due to its large active space.

4.6 Discussions

The present chapter addresses decomposition behavior of the furazan based energetic material, DAAF and its model systems, DAF and furazan upon electronic state excitations. With regard to the furazan based energetic systems, DAAF has been our major focus thus far. We have observed only NO from any of these systems, and we conclude that it is the major initial product in their excited electronic state decomposition. NH_2 is not observed as a secondary decomposition product both in TOFMS and LIF experiments. In our experiments, each parent molecule is excited to its excited electronic state using different excitation wavelengths (226 nm, 236 nm and 248 nm) that also correspond to the resonance $A^2\Sigma(v'=0) \leftarrow X^2\Pi(v''=0,1,2)$ transitions

of NO. The NO product from DAAF displays similar cold rotational distributions (20 K) at all three excitation wavelengths (226 nm, 236 nm and 248 nm). Similar rovibronic spectral structures for product NO from DAAF at different excitation wavelengths indicate that excited electronic state decomposition of DAAF follows a single, excitation wavelength independent, dissociation channel. The model systems, on the other hand, show excitation wavelength dependent dissociation channels. For example, dissociation of furazan at 236 nm and DAF at 248 nm renders hot rotational distributions for the NO product, whereas excitation of furazan at 226 nm and DAF at 226 and 236 nm yields cold rotational distributions for the NO product. Thus, we conclude that the excited electronic state decomposition of the energetic material DAAF takes place through the same pathway at the three excitation wavelengths used in this experiment, but the excited electronic state decomposition of the model systems (DAF and furazan) takes place through two different dissociation channels depending on excitation wavelengths. This difference in behavior can only be rationalized by the fact that DAAF must have dissociative excited states which can provide a barrierless single deactivation channel for excited state decomposition. For the model systems, on the other hand, a barrier in the excited state decomposition pathway must exist which can alter the dissociation channel from the excited state. As an example, excitation of furazan and DAF at 226 nm (5.5 eV) can surmount an energy barrier to provide a rotationally cold (20K) distribution for the NO product, and excitation of furazan at 236 nm (5.26 eV) and DAF at 248 nm (5.0 eV) does not provide sufficient energy to surmount that barrier. Eventually they follow different dissociation channels, providing hot NO rotational distributions. Moreover, the threshold excitation energies for the two

different dissociation channels of the model systems must be between 5.5 eV (~ 226 nm) and 5.25 eV (~ 236 nm) for furazan and 5.25 eV (~ 236 nm) and 5.0 eV (~ 248 nm) for DAF. To get theoretical support and understanding for these experimental observations, the evolution pathways from excited electronic states with respect to the relevant reaction coordinates have to be known. We have therefore explored the potential energy surfaces for the model systems furazan and DAF, shown in Figure 4.9 A and B. Note that two nonadiabatic dissociation channels are along two different nuclear co-ordinates and CASSCF calculated energies are ~ 1 -2 eV off from the MP2 correlated CASSCF energies.

Conical intersections are now firmly established to be the key features in the excited electronic state chemistry of the polyatomic molecules.²⁹⁻³¹ The concept of a conical intersection was first introduced by Wigner³² and has been now recognized as essential for describing the dynamics and mechanisms for deactivation of a vast range of polyatomic molecules from their excited electronic states to their ground electronic surface.³³⁻³⁷ One of their most important implications is the rapid and efficient internal conversion from upper to lower electronic state surfaces through radiationless transitions. This radiationless transition through a conical intersection involves rapid conversion of electronic energy belonging to the upper electronic state to vibrational energies (thermal energies) of the lower electronic state. As mentioned in the Theoretical Results section, the excitation wavelengths used in our experiment correspond to the transition to the $S_2(\pi,\pi^*)$ excited state of the furazan hetero-aromatic rings, and in particular, 226 nm excitation corresponds to the absorption maximum (vertical excitation) for the $S_2(\pi,\pi^*)$ excited state of furazan. Thus, for furazan,

existence of the $(S_1/S_0)_{CI,a}$ conical intersection (see Figure 4.9A) at almost the same energy as that of the absorption maximum of the spectroscopically active $S_2(\pi,\pi^*)$ state, which indicates that due to excitation to the $S_2(\pi,\pi^*)$ state at 226 nm, electronic energy can be rapidly thermalized through an almost barrierless nonadiabatic ring contraction dissociation pathway from the FC point (absorption maximum) of the $S_2(\pi,\pi^*)$ state through the $(S_1/S_0)_{CI,a}$ conical intersection. This dynamical process will generate NO product with cold rotational distributions, as the unstable normal mode of vibration associated with the relevant transition state on the ground electronic state surface do not generate a resultant torque on the NO moiety during dissociation of the parent molecule. In this dynamical process, the adiabatic state switch from the spectroscopic (π,π^*) to the (n,π^*) state must occur by crossing the $(S_2/S_1)_{CI}$ conical intersection.

At 236 nm excitation, on the other hand, furazan cannot surmount the energy barrier for the $(S_1/S_0)_{CI,a}$ conical intersection since 236 nm excitation energy is about 0.25 eV lower than that of 226 nm. Rather this electronic energy eventually gets thermalized by the repopulation of other vibronically active modes through IVR; these other modes can follow another nonadiabatic dissociation channel through the $(S_1/S_0)_{CI,b}$ conical intersection after crossing the $(S_2/S_1)_{CI}$ conical intersection. This ring opening decomposition pathway can result in a rotationally hot distribution of NO, as the relevant TS on the ground electronic state surface following the $(S_1/S_0)_{CI,b}$ conical intersection is associated with an unstable torsional degree of freedom, which generates a torque on the NO moiety during dissociation of the parent molecule. Thus, the proposed mechanism suggests that excited electronic state decomposition of furazan at 226 nm and 236 nm excitations involves two different nonadiabatic dissociation

pathways: ring contraction mechanism through $(S_1/S_0)_{CI,a}$ and ring opening mechanism through $(S_1/S_0)_{CI,b}$. Both mechanism yields NO as initial decomposition product. The NO product due to excited electronic state decomposition of furazan at 226 nm excitation is expected to be rotationally cold and at 236 nm excitation is expected to be rotationally hot, in good agreement with experimental observation.

In addition, we conclude that, when the molecule has high enough energy to surmount the energy barrier for the $(S_1/S_0)_{CI,a}$ conical intersection, it undergoes nonadiabatic dissociation predominately following the $(S_1/S_0)_{CI,a}$ conical intersection not through the $(S_1/S_0)_{CI,b}$ conical intersection. One reason for this conclusion is that if 226 nm excitation can access both nonadiabatic decay channels through $(S_1/S_0)_{CI,a}$ and $(S_1/S_0)_{CI,b}$ conical intersections with equal probabilities, then one should observe hot rovibronic structure for NO from 226 nm excitation of furazan convoluted with cold rovibronic structures in the ns laser experiments. Instead, we observe only a cold rotational distribution of NO from decomposition of furazan at 226 nm excitation. If the molecule, on the other hand, does not have sufficient energy to surmount the energy barrier for the $(S_1/S_0)_{CI,a}$ conical intersection, it will eventually follow the other nonadiabatic decay channel crossing the $(S_1/S_0)_{CI,b}$ conical intersection following internal conversion through the $(S_2/S_1)_{CI}$ conical intersection rendering hot rotational distribution for the NO product. Wavepacket dynamics calculations and femtosecond pump-probe experiments for furazan are needed to confirm the influence of the limiting factors, adiabatic state switching and IVR on the proposed decomposition dynamics of furazan from its excited electronic state.

A similar $(S_1/S_0)_{CI,a}$ conical intersection (shown in Figure 4.9B) for DAF is found ~ 1 eV (within the calculated energy uncertainty at the CASMP2//CASSCF level) in energy below its vertical excitation energy. Thus, excitation of DAF at both 226 nm and 236 nm can follow the nonadiabatic dissociation pathway through the $(S_1/S_0)_{CI,a}$ conical intersection, but 248 nm excitation of DAF cannot surmount that energy barrier. Rather DAF dissociates following 248 nm excitation along the $(S_1/S_0)_{CI,b}$ conical intersection resulting in a rotationally hot distribution of NO. Thus proposed mechanism suggests that excited electronic state decomposition of DAF at 226 nm and 236 nm excitations involves ring contraction nonadiabatic dissociation pathway yielding only rotationally cold distribution of the NO product. At 248 nm excitation of DAF, another nonadiabatic dissociation pathway is opened rendering a rotationally hot distribution of NO. This mechanism is in good agreement with experimental observation.

As DAAF has generated only rotationally cold distributions of NO product due to excitation at three different excitation energies, we extrapolate that the excited electronic states of DAAF are dissociative in nature, and that the DAAF conical intersection between (n,π^*) excited state and ground electronic state, $(n,\pi^*/gs)_{CI}$ (similar to the $(S_1/S_0)_{CI,a}$ for DAF and furazan) is even lower in energy than that for DAF. Thus the suggested DAAF $(n,\pi^*/gs)_{CI}$ conical intersection can be readily accessible by electronic excitations at all of the three excitation wavelengths used in our experiment. This energetically accessible $(n,\pi^*/gs)_{CI}$ conical intersection can provide DAAF a very efficient, unique, and single pathway to release its entire chemical energy from random electronic excitations to its (π,π^*) excited electronic state during the detonation of this

energetic material simply initiated by compression or shockwaves. The model systems, on the other hand, suffer from not having an efficient single pathway to release their entire chemical energy during excited electronic state decompositions of these species. One pathway for the model systems provides rotationally cold NO product through contraction mechanism; another provides rotationally hot NO product through ring opening mechanism. Thereby, the energy barrier for the $(n,\pi^*/gs)_{CI}$ conical intersection with respect to excitation wavelengths plays a crucial role in the decomposition mechanism of these molecules, and thus DAAF, being an energetic material, behaves differently from its nonenergetic model systems. The pump-probe transient for the NO product at resonant wavelength indicates that the decomposition dynamics of DAAF falls within the time scale of our femtosecond laser pulse duration (180 fs).

4.7 Conclusions

This chapter focuses the excited electronic state decomposition behavior of DAAF and its model systems, which has been investigated via ns energy resolved and fs time resolved spectroscopy. Both DAAF and its model systems generate NO as an initial decomposition product; however, at the ns laser excitation wavelengths, vibrational and rotational distributions of the NO product are quite different. DAAF generates the NO product with only cold rotational (20 K) and hot vibrational (1260 K) distributions that are independent of excitation wavelengths. On the contrary, the model systems generate different rotational distributions for NO depending on the excitation wavelengths employed for excited electronic state decomposition of the parent molecules. Based on the experimental observations and CASSCF calculations we conclude that excited electronic state decomposition of DAAF occurs through a unique,

single, nonadiabatic ring contraction dissociation channel that is independent of excitation wavelengths. The model systems (DAF and furazan) dissociate through two different, excitation wavelength dependent, nonadiabatic dissociation channels: ring contraction and ring opening. In this case, the energy barrier for $(S_1/S_0)_{CI,a}$ conical intersection with respect to excitation energy plays a crucial role in the initial excited electronic state decomposition of the model systems. The dynamics of NO generated from DAAF is found to fall within the time scale of our laser pulse duration (180 fs). NH_2 is not observed as secondary decomposition product of either DAAF or DAF.

4.8 Acknowledgements

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CHAPTER 5

Unimolecular Decomposition of Tetrazine-N-oxide Based High Nitrogen Content Energetic Materials from Excited Electronic States

Work presented in this chapter is published in “Bhattacharya, A.; Guo, Y. Q.; Bernstein, E. R. *J. Chem. Phys.* **2009**, *131*, 194304.” Yuanqing and I worked together on the experiments and I worked independently on the theoretical calculations.

5.1 Introduction

Recently, high nitrogen content energetic materials have received increased attention due to their novel energetic and explosive properties.¹⁻⁹ A high nitrogen content energetic material is a compound with a large number of N-N linkages. Increasing the nitrogen content at the expense of carbon/hydrogen content in the energetic molecule has several advantages:¹ (1) the low percentage of carbon and hydrogen allows a good oxygen balance and enhances crystal density, and (2) utilization of the N-N moiety in the energetic species increases its heat of formation (enthalpy of formation often exceeds 400 kcal/mol). These unique characteristics of nitrogen rich energetic materials are critical parameters for enhancement of their energy storage capabilities. Additionally, a high percentage of their decomposition product is expected to be the colorless, inert, nontoxic, and environmentally friendly, nitrogen

molecule. These features can also facilitate the formation of smoke free, ‘reduced-signature’ propellants which are useful for military applications. Therefore, nitrogen rich energetic materials are promising substitutes for the more traditional nitramine and nitro containing systems and would be more acceptable than these traditional energetic materials for both industrial and military use in the near future.¹⁰

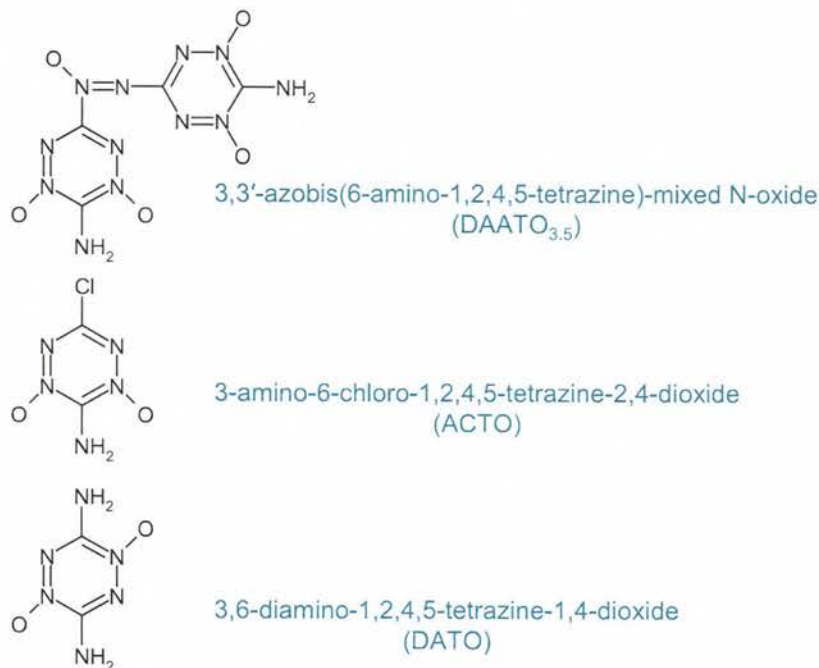


Figure 5.1: Chemical structures of tetrazine-N-oxide based energetic molecules: DAATO_{3.5}, ACTO, and DATO.

Tetrazine-N-oxide, a high nitrogen content molecule, is one of the many nitrogen rich heterocyclic frameworks on which a number of high nitrogen content energetic materials are based. For instance, 3,3'-azobis(6-amino-1,2,4,5-tetrazine)-mixed N-oxides (DAATO_{3.5}, structure illustrated in Figure 5.1) is a tetrazine-N-oxide based nitrogen rich energetic material, which has recently received increased attention due in large part to its extremely high burn rate and low dependency on pressure.^{6,8} This

molecule has an average stoichiometric oxygen content of about 3.5. Another two important tetrazine-N-oxide based energetic molecules are 3-amino-6-chloro-1,2,4,5-tetrazine-2,4-dioxide (ACTO, structure in Figure 5.1) and 3,6-diamino-1,2,4,5-tetrazine-1,4-dioxide (DATO, structure in Figure 5.1),⁹ which have been relatively unexploited for use as energetic materials. DAATO_{3.5} and ACTO differ from DATO mainly by the relative position of the oxygen atom attached to the tetrazine ring. DAATO_{3.5} and ACTO possess a tetrazine-2,4-dioxide moiety, whereas DATO has a tetrazine-1,4-dioxide moiety. From an energetic point of view, two potential advantages of tetrazine-N-oxides over a bare tetrazine ring can be mentioned.¹¹ First, formation of an N-oxide of a heterocyclic ring enhances the aromaticity in the ring, which makes it less sensitive to destructive stimuli (e.g., friction). Second, N-oxides provide a better oxygen balance in energetic materials, and their alternating charges help increase the solid density by enabling better crystal packing.

Two studies of the basic sensitivity and performance of tetrazine-N-oxide based energetic materials have appeared in literature;^{6,8} however, the unimolecular decomposition of these molecules has not been studied thus far. Excited electronic states are proposed to play an important role in the shock wave decomposition of energetic materials:¹² excited electronic states can be created by decreasing the HOMO-LUMO energy gap via compression from the wave front of a shock wave, and by the shearing of crystal planes.¹³ Therefore, elucidation of detailed fundamental steps in the unimolecular decomposition of tetrazine-N-oxide based energetic molecules from their low lying excited electronic states is essential for understanding, controlling, and enhancing the detonation performances of these materials.

In this chapter, we focus on understanding the decomposition mechanisms and dynamics of DAATO_{3.5}, DATO, ACTO under molecular beam conditions. Thus far, NO is experimentally observed to be an initial decomposition product from their excited electronic states; nonetheless, we do not exclude the possibility of generating N₂ as another initial decomposition product from these molecules. The NO product is rotationally cold (20 K), but vibrationally hot (1200 K), for tetrazine-2,4-oxide based molecules such as DAATO_{3.5} and ACTO, while the NO product is rotationally hot (50 K), but vibrationally cold (only (0-0) transition of NO is observed), for tetrazine-1,4-dioxide based molecules such as DATO. Therefore, the relative position of the oxygen atoms attached to the tetrazine ring evidences a significant effect on the final internal energy distribution among products following excited electronic state decomposition of tetrazine-N-oxide based energetic molecules. Experimentally, we confirm that N₂O is not an intermediate precursor for the NO product. Moreover, the decomposition behavior of tetrazine-N-oxides is different from that of the bare tetrazine ring, which produces N₂ and HCN as decomposition products through a concerted triple decomposition mechanism.¹⁴ *Ab initio* calculations at the CASMP2/CASSCF level of theory are employed to explore the relevant excited electronic state potential energy surfaces and conical intersections for DAATO_{3.5}, DATO and ACTO. Based on these calculations, and the experimental observations, we propose that a novel ring contraction mechanism through an (S₁/S₀)_{CI} conical intersection is involved in the excited electronic state decomposition of tetrazine-N-oxide based molecules. The NO product is the result of this mechanism. Thus, present results provide several detailed

insights into the unimolecular decomposition behavior of the tetrazine-N-oxide based energetic molecules from their excited electronic states.

5.2 Experimental methods

The experimental setup consists of ns laser systems, a supersonic jet expansion pulsed nozzle, and a time of flight mass spectrometer (TOFMS) chamber, described in detail elsewhere.¹⁵⁻²¹ In this work, a single pump/probe laser beam with 8 ns time duration at three wavelengths (226 nm, 236 nm and 248 nm) is used both to initiate dissociation of tetrazine-N-oxide based molecules and to detect NO following a one color (1+1) R2PI (resonance enhanced two photon ionization) scheme [$A^2\Sigma (v'=0) \leftarrow X^2\Pi (v''=0,1,2)$ and $I \leftarrow A$ transitions] through a TOFMS. The three UV laser wavelengths used in these experiments are generated by a pulsed dye laser, pumped by the second harmonic (532 nm) of the Nd:YAG laser's fundamental output (1.064 μm), in conjunction with a nonlinear wavelength extension system. Typical pulse energy of the UV laser is 200-600 $\mu\text{J/pulse}$ depending on the exact wavelength of interest for a one-color experiment, which gives a laser beam intensity (I) ~ 1.3 to $4 \times 10^7 \text{ W/cm}^2$ for an 8 ns pulse duration at a focused beam diameter of 0.5 mm.

The isolated gas phase DAATO_{3,5}, ACTO, DATO molecules are produced through a combination of matrix assisted laser desorption (MALD) and supersonic jet expansion. The nozzle employed for the sample beam generation and the procedure for the sample drum preparation are the same as those used for our previous energetic materials experiments.¹⁵⁻¹⁸ A 1% N₂O in He gas mixture is prepared for the calibration of NO from decomposition of N₂O at the excitation wavelengths mentioned above.

The experiment is run at a repetition rate of 10 Hz. The timing sequence for the pulsed nozzle, ablation laser, and ionization laser is controlled by a time delay generator (SRS DG535). The molecular beam is perpendicularly crossed by the UV laser beam that is focused to a spot size of about 0.5 mm at the ionization region of a time of flight mass spectrometer. A background pressure of 1×10^{-5} Torr is maintained in the vacuum chamber during the experiment. Ion signals are detected by a microchannel plate detector (MCP). Signals are recorded and processed on a PC using a box car averager (SRS SR 250) and an ADC card (Analog Devices RTI-800). DAATO_{3,5}, ACTO, and DATO are supplied by Los Alamos National Laboratory (D. E. Chavez) and used without additional purification.

5.3 Theoretical methods

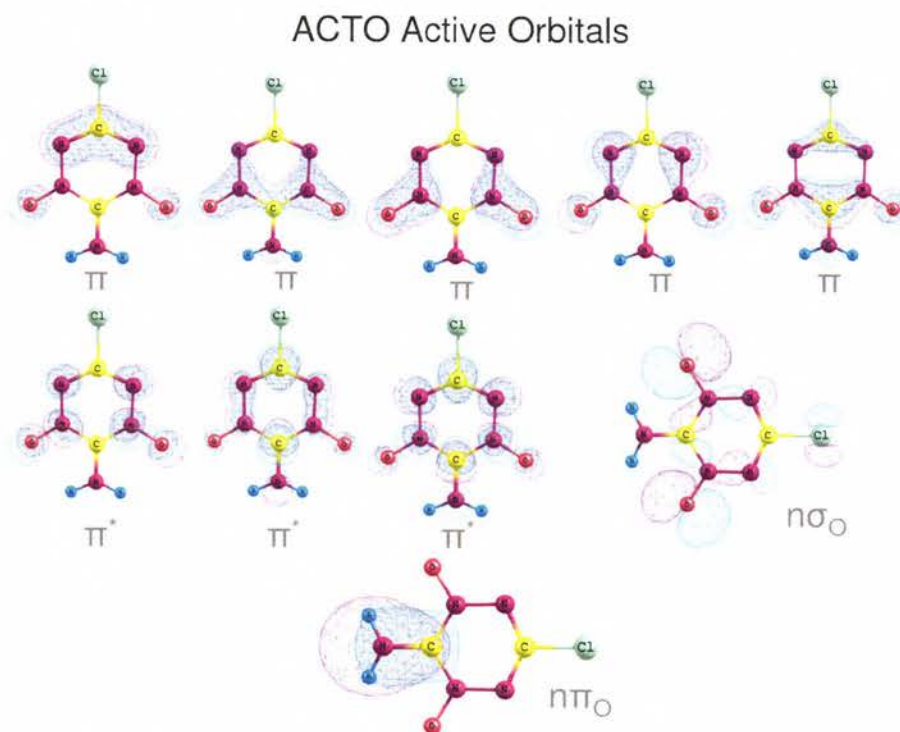


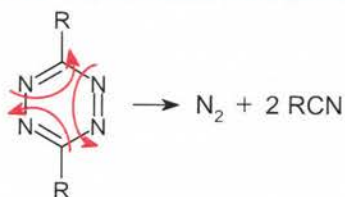
Figure 5.2: Orbitals used in the active space of CASSCF calculations for ACTO. The (10,8) active space comprises only bonding and antibonding π orbitals. The (14,10) active space includes two more nonbonding orbitals.

Potential energy surface calculations and geometry optimizations for ACTO and DATO are performed at the CASSCF/6-31G(d) level of theory with the Gaussian03 program.²² No symmetry restrictions are applied during the calculations. For calculations on the S_1 excited state potential energy surface of DATO and ACTO, an active space comprising 14 electrons in 10 orbitals, denoted as CASSCF(14,10), is used. Orbitals used in the CASSCF(14,10) calculations are bonding π , antibonding π^* , and two non bonding orbitals, which are shown in Figure 5.2 for ACTO.

Vertical excitation energies are computed by state-averaging over the ground state and two successive singlet excited states with equal weights. For reliable estimation of vertical excitation energies, MP2 correlated CASSCF energies are also calculated. As the S_1 excited electronic surface for both ACTO and DATO is an (n,π^*) excited state, the active space for the optimization of the critical points (local minimum and conical intersections) on the S_1 surface should include all the bonding and antibonding π orbitals and two in-plane O nonbonding $n\sigma_O$ orbitals. The geometries of the critical points are optimized with state averaging over S_0 and S_1 states with equal weights. On the other hand, as the S_2 and S_3 excited electronic surfaces have a (π,π^*) character, critical points (local minimum, denoted as $(\pi,\pi^*)_{\text{Min}}$, and conical intersections for S_2 and S_3 are optimized with a reduced active space of (10,8), including only π bonding and antibonding orbitals. Then single point energies are calculated for these critical points on the S_2 and S_3 surfaces to obtain relative energy differences with large active space (14,10) for DATO and ACTO, respectively. Transition state (TS) structures are characterized by analytical frequency calculations.

5.4 Experimental Results

• Tetrazine Based Molecules:

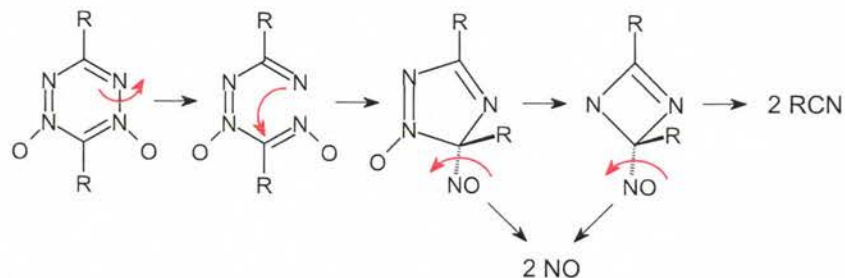


• Tetrazine-N-oxides Based Molecules:

(a) N_2O elimination



(b) Ring contraction, leading to NO elimination



(c) Meisenheimer rearrangement, leading to N_2 elimination

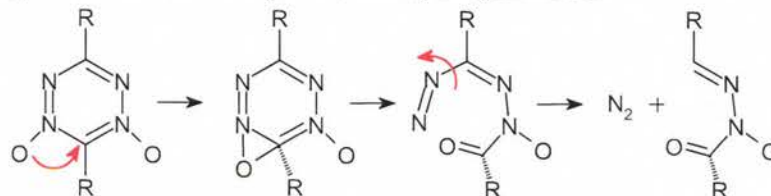


Figure 5.3: Different possible decomposition pathways of tetrazine and tetrazine-N-oxide based molecules.

To elucidate decomposition mechanism and dynamics of tetrazine-N-oxide based energetic molecules, the parent molecule of interest is excited to an excited electronic state by absorption of a single UV photon at three excitation wavelengths (226 nm, 236 nm and 248 nm). The parent molecules decompose into products through specific decomposition pathways. Different possible decomposition pathways of

tetrazine-N-oxides based molecules are illustrated in Figure 5.3. Tetrazine-N-oxide based molecules potentially can generate a number of initial products such as N_2O , NO, and N_2 through concerted or step wise ring opening, ring contraction, and Meisenheimer rearrangement mechanisms, respectively. Nitric oxide (NO), however, is experimentally observed to be an initial dissociation product in the excited electronic state decomposition of DAATO_{3,5}, ACTO, and DATO.

The NO product is probed using a one-color (1+1) R2PI detection scheme through TOFMS. The three excitation wavelengths used in this work also correspond to the resonance (0-0), (0-1), and (0-2) vibronic bands of the $A^2\Sigma^+ \leftarrow X^2\Pi$ electronic transitions of the NO product, respectively. By scanning the ns laser excitation wavelength, a (1+1) R2PI rotationally resolved spectrum of the NO product from different parent molecules is recorded. The parent molecule has continuous absorption in these wavelength regions. Although the matrix assisted desorption technique (MALD) technique is a good method to place easily fragmented, fragile molecules in the gas phase without fragmentation, great effort is taken in our previous and present work to ensure that the sample molecules are not fragmented in the ablation process.¹⁵⁻

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(1+1) R2PI spectra of the three vibronic transitions, $A^2\Sigma^+(v'=0) \leftarrow X^2\Pi(v''=0,1,2)$ of the NO product observed from excited electronic state decomposition of DAATO_{3,5} are shown in Figure 5.4. The most intense feature in each spectrum of NO can be assigned as the (Q₁₁+P₁₂) band head of each vibronic band,²³ and the less intense features within each spectrum are due to other rovibronic transitions. Spectral simulations based on Boltzmann population distributions for the

three vibronic transitions produce similar rotational temperatures (~ 20 K). The vibrational temperature of the NO product from DAATO_{3.5} can also be obtained by simulating the relative intensities among the observed vibronic bands using a Boltzmann population distribution analysis and Franck-Condon factors. By comparing the experimental data with simulations at different vibrational temperatures, the vibrational temperature of the NO product from DAATO_{3.5} is estimated to be 1200 K.

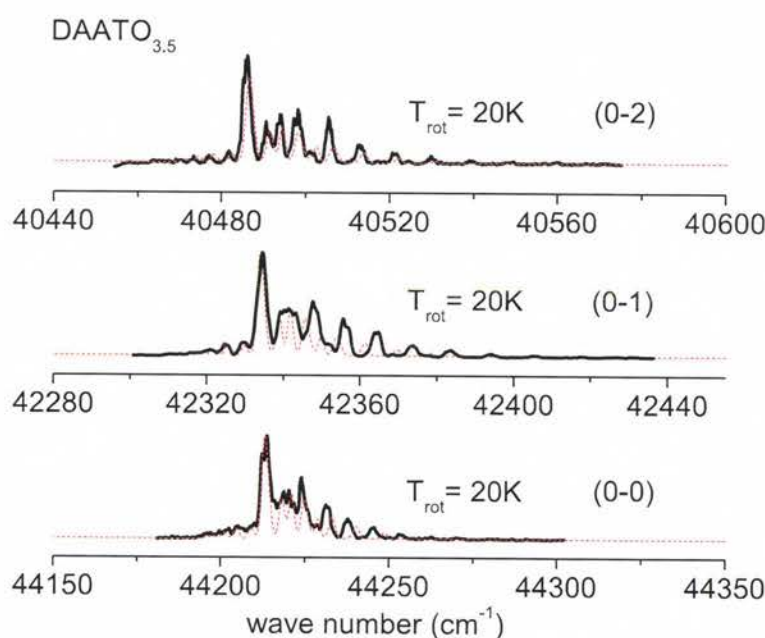


Figure 5.4: One color (1+1) R2PI spectra of the vibronic transitions $A^2\Sigma^+(v'=0) \leftarrow X^2\Pi(v''=0,1,2)$ of the NO product from the excited electronic state decomposition of DAATO_{3.5}. Rotational temperature simulations with a Boltzmann population distribution show that the three observed vibrational levels on the ground electronic states have a similar rotational temperature of ca. 20 K.

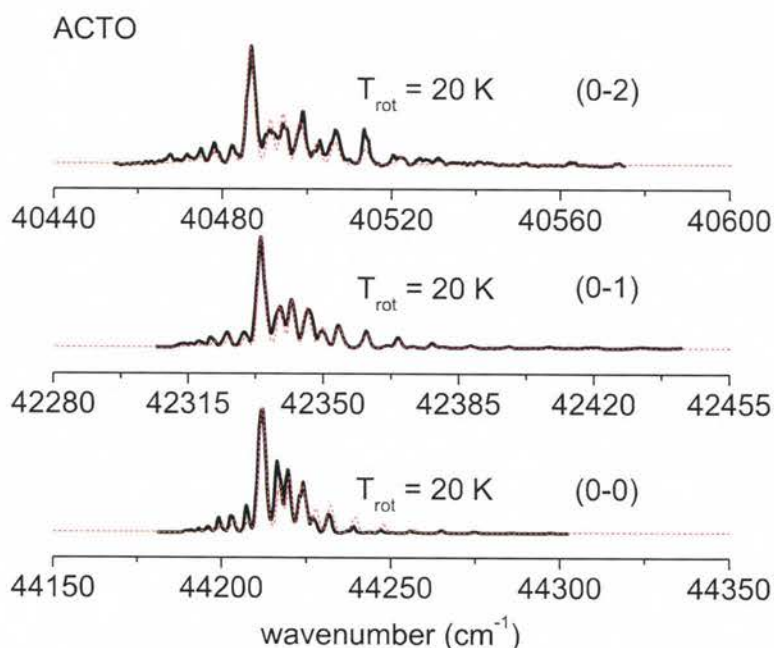


Figure 5.5: One color (1+1) R2PI spectra of the vibronic transitions $A^2\Sigma^+(v'=0) \leftarrow X^2\Pi(v''=0,1,2)$ of the NO product from the excited electronic state decomposition of ACTO. Rotational temperature simulations with a Boltzmann population distribution show that the three observed vibrational levels on the ground electronic states have a similar rotational temperature of ca. 20 K

Similar (1+1) R2PI spectra of three vibronic transitions, $A^2\Sigma^+(v'=0) \leftarrow X^2\Pi(v''=0,1,2)$ of the NO molecule obtained from excited electronic state decomposition of ACTO are shown in Figure 5.5. The (0-0), (0-1), and (0-2) vibronic bands of the NO product from ACTO show similar rotational patterns to those of the NO product from DAATO_{3,5}, and the rotational temperature of these bands is also about 20 K.

The excited electronic state decomposition of the DATO also generates an NO product, however, with only a $v''=0$ population. The (1+1) R2PI spectrum of the (0-0) vibronic band of the NO product from DATO is illustrated in Figure 5.6, which shows a hotter rotational pattern with a temperature of about 50 K. Thus, distinctly different

rovibrational distributions of the NO product are observed from DATO and ACTO. The major structural difference between these two molecules is the relative position of the oxygen atoms attached to the tetrazine ring. Therefore, the relative position of oxygen atoms in tetrazine-N-oxide based energetic molecules is proposed to play an important role in their energetic and explosive behavior.

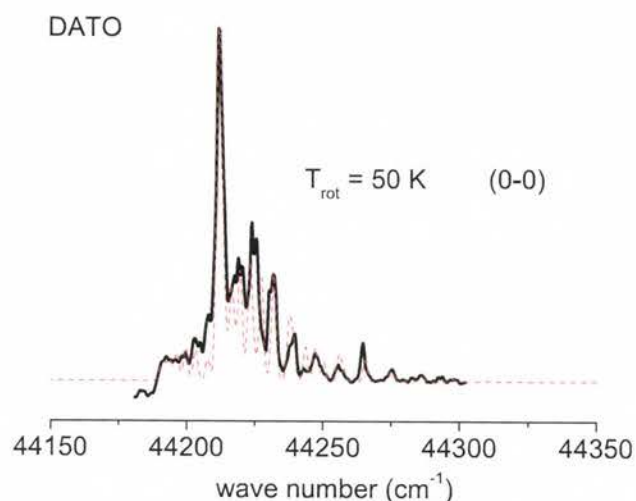


Figure 5.6: One color (1+1) R2PI spectra of the vibronic transitions $A^2\Sigma^+(v'=0) \leftarrow X^2\Pi(v''=0)$ of the NO product from the excited electronic state decomposition of DATO. Rotational temperature simulations with a Boltzmann population distribution estimates a rotational temperature of ca. 50 K

DAATO_{3,5}, ACTO, and DATO are N-oxide derivatives of the tetrazine aromatic heterocyclic ring. Photodissociation of the tetrazine molecule has been intensively investigated both experimentally and theoretically.¹⁴ To date, N₂ is undoubtedly corroborated to be the initial photodecomposition product (see Figure 5.3); however, different experiments support different mechanisms (either concerted or step-wise) for this photodissociation reaction. Considering a similar decomposition mechanism, the immediate discernible photodissociation product for tetrazine-N-oxides is predicted to

be N_2O (see Figure 5.3), which in principle could be an intermediate precursor for the NO product observed in the experiment. Thus, a comparison of the rotational and vibrational distributions of the NO product from photolysis of N_2O to that from photolysis of $\text{DAATO}_{3.5}$, ACTO , and DATO is performed, so that one can determine whether N_2O could be an appropriate intermediate.

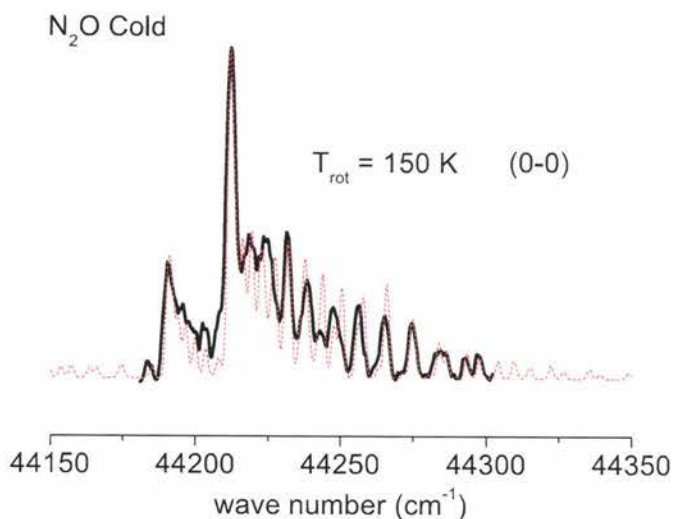


Figure 5.7: One color (1+1) R2PI spectra of the vibronic transitions $A^2\Sigma^+(v'=0) \leftarrow X^2\Pi(v''=0)$ of the NO product from the excited electronic state decomposition of N_2O . Rotational temperature simulations with a Boltzmann population distribution estimates a rotational temperature of ca. 150 K

(1+1) R2PI spectrum of NO from photolysis of N_2O in the NO $A^2\Sigma^+(v'=0) \leftarrow X^2\Pi(v''=0)$ transition region is presented in Figure 5.7. Only the (0-0) vibronic band of the NO product is observed from photolysis of N_2O at 226 nm photoexcitation, and the spectrum is characterized by a rotational temperature of about 150 K. Assuming N_2O is an intermediate precursor for the NO product in the excited electronic state decomposition of tetrazine-N-oxide based molecules, the final NO

product should present similar or hotter rotational or vibrational distributions compared to that from N_2O gas, which is cooled before photolysis under molecular beam conditions. NO from photolysis of all tetrazine-N-oxide based energetic molecules is, however, rotationally colder and vibrationally hotter than, or similar to, that from N_2O gas. These differences indicate that N_2O cannot be an intermediate precursor for the NO product in the excited electronic state decomposition of tetrazine-N-oxides. Instead, a ring contraction mechanism is proposed to be the mechanism of NO elimination from these molecules. Furthermore, one can also infer that excited electronic state decomposition behavior of tetrazine-N-oxide is essentially different from that of bare tetrazine.

5.5 Theoretical Results

For the assessment of which excited electronic states of tetrazine-N-oxide based molecules are relevant to our experimental observations, a comparison between the computed vertical excitation energies and experimental excitation energies is performed. The vertical excitation energies (E_{vert}) for ACTO, computed at the CASSCF(10,8)/6-31G(d) optimized Franck-Condon geometry (FC geometry at ground state minimum) of C_1 symmetry including only bonding and antibonding π orbitals in the active space, are listed in Table 5.1.

Table 5.1: Calculated Vertical Excitation Energies (E_{vert}) and Relative Energies of the Conical Intersections and Transition States with Respect to the Energy of FC Geometry, Optimized at CASSCF(10,8)/6-31G(d).

Compound	State/CI	Configurations	$E_{\text{vert}}/\Delta E$ (eV) ^a	E_{vert} (Expt., eV) ^b
ACTO	S ₁ (FC)	(n, π^*)	3.87 (3.80)	2.91
	S ₂ (FC)	(π,π^*)	5.14 (4.59)	4.14
	S ₃ (FC)	(π,π^*)	5.90 (5.52)	5.50
	(S ₁ /S ₀) _{CI}		2.45	
	(S ₂ /S ₁) _{CI}		4.85	
	(S ₃ /S ₂) _{CI}			
	TS(S ₀)		2.80	
	TS(S ₁)		4.47	
DATO	S ₁ (FC)	(n, π^*)	3.56 (3.55)	2.72
	S ₂ (FC)	(π,π^*)	4.79 (4.45)	4.58
	S ₃ (FC)	(π,π^*)	6.18 (5.92)	6.17
	(S ₁ /S ₀) _{CI}		2.50	
	(S ₂ /S ₁) _{CI}		2.81	
	TS(S ₀)			
	TS(S ₁)			

^anumbers within brackets give the MP2 correlated CASSCF energies (eV)

^bexperimental absorption maxima for each compound obtained from UV-VIS absorption spectra (see Figure 5.S1 in Supplementary Information)

The CASSCF calculations show that the three lowest lying excited electronic states (S₁, S₂, and S₃) for ACTO possess vertical excitation energies of 3.87, 5.14, and 5.9 eV, respectively. The calculated vertical excitation energies of the S₂ and S₃ states at the MP2 correlated CASSCF level of theory are 4.59 and 5.52 eV, respectively, which are in good agreement with the experimental absorption maxima of 4.14 and 5.5 eV (see Figure 5.S1 of Supplementary Information for UV-VIS absorption spectrum of ACTO); however, the calculated vertical excitation energy (3.8 eV) of the S₁ state even at MP2 correlated CASSCF level of theory is in poor agreement with the experimental

absorption maximum of 2.9 eV. In order to improve the calculation for the vertical excitation energy associated with S_1 state, a larger (14,10) active space including two more non bonding orbitals is necessary. The vertical excitation energy of the S_1 state at the CASSCF(14,10)/6-31G(d) level of theory is calculated to be 3.4 eV, which is in better agreement with the experimental absorption maximum of 2.9 eV. The calculated vertical excitation energies for S_2 and S_3 states change slightly with a (14,10) active space. In addition, calculation at the CASSCF(14,10)/6-31G(d) level of theory also shows that the S_1 state includes significant mixing between (n,π^*) and (π,π^*) configurations. The relative weights of the (π,π^*) and (n,π^*) configurations to the S_1 state are computed to be 30% and 70%, respectively. The calculated vertical excitation energies of the S_2 and S_3 states for DATO (see Table 5.1) at both CASSCF and MP2 correlated CASSCF(10,8) levels of theory are also in good agreement with the experimental absorption maxima; however, considerable mismatch also exists between theory and experiment for vertical excitation energy of S_1 state.

Therefore, the CASSCF computation including only bonding and antibonding π orbitals in the active space provides a reasonable treatment of the S_3 and S_2 excited electronic states; however, inclusion of nonbonding orbitals ($n\sigma_O$ and $n\pi_N$) in the active space is necessary to explore the S_1 potential energy surface of ACTO and DATO. Moreover, dynamical correlation (omitted in a CASSCF calculation but included in MP2 correlated CASSCF calculation) is not a major contributor to the low-lying excited electronic states of ACTO and DATO.

Comparison of the experimental excitation energies (5.5 eV at 226 nm, 5.26 eV at 236 nm, and 5.00 eV at 248 nm) used in this work with the calculated vertical

excitation energies at the MP2 correlated CASSCF level of theory indicates that these UV-photoexcitations of ACTO and DATO primarily populate the Franck-Condon modes of the S_3 or S_2 surface.

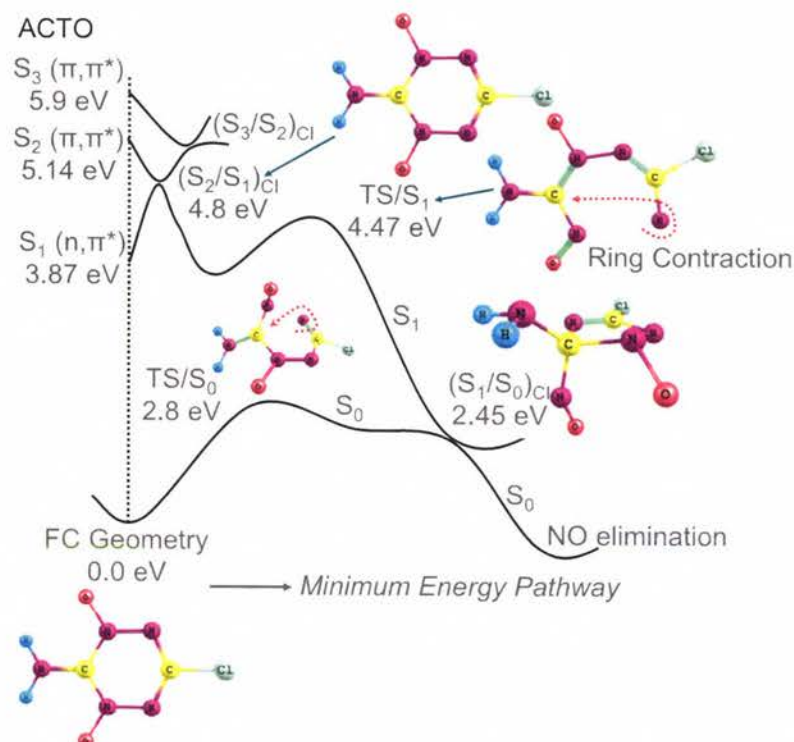


Figure 5.8: One dimensional projection of the multidimensional singlet electronic potential energy surfaces of ACTO computed at CASSCF(10,8)/6-31G(d) level of theory. Geometry near the $(S_1/S_0)_{CI}$ supports a ring contraction mechanism for excited electronic state decomposition of ACTO, which finally results in NO elimination. Note that ring contracted form of ACTO near the $(S_1/S_0)_{CI}$ has nearly linear C-NO moiety attached to the triazole ring, which can finally generate a rotationally cold NO product.

A schematic one-dimensional projection of the multidimensional singlet potential energy surfaces (S_0 , S_1 , S_2 , and S_3) of ACTO with locations and structures of different critical points and conical intersections following the ring contraction pathway is plotted in Figure 5.8. Following vertical excitation to the FC point of the S_3 surface, ACTO can undergo rapid nonadiabatic internal conversion from S_3 to S_2 through the

$(S_3/S_2)_{CI}$ and thereafter, from S_2 to S_1 through the $(S_2/S_1)_{CI}$ conical intersection. These nonadiabatic state changes occur without significant change in nuclear configuration (molecular geometry). This process is energetically accessible from the FC point of the S_3 surface, because practically no barriers exist along the minimum energy pathway (MEP) for this process.

Following internal conversion to the S_1 surface, under isolated molecular beam conditions, the excitation energy is stored in the vibrational degrees of freedom of the molecule on the S_1 surface. Therefore, a ring contraction excited electronic state process can be initiated on the S_1 surface of ACTO. On the S_1 surface, the activation barrier (at 4.47 eV with respect to the S_0 FC point, see Figure 5.8) for ring contraction of ACTO can easily be surmounted because the excess energy stored in the vibrational degrees of freedom of the S_1 molecule, following radiationless internal conversion of the ACTO to the S_1 surface, is sufficient to surmount the barrier. Following this transition state, the molecule is directed to the $(S_1/S_0)_{CI}$ and relaxes back to S_0 surface upon which NO elimination takes place with no activation barrier. Thereby, in brief, the ring contraction of the electronically excited ACTO, which leads to the formation of ground state NO as an initial decomposition product, begins on the S_1 surface and develops through the $(S_1/S_0)_{CI}$.

A similar one-dimensional projection of the multidimensional singlet potential energy surfaces (S_0 , S_1 , and S_2) of DATO with locations and structures of different critical points and conical intersections following the ring contraction pathway is plotted in Figure 5.9. Following vertical excitation to the FC point of the S_2 surface, DATO can undergo rapid nonadiabatic internal conversion from S_2 to S_1 through the

$(S_2/S_1)_{CI}$ conical intersection. This internal conversion to the S_1 surface, under isolated molecular beam conditions, stores the remainder of the excitation energy in the vibrational degrees of freedom of the molecule on the S_1 surface, which can initiate a ring contraction excited electronic state process. Following the ring contraction transition state (RCTS), the molecule is directed to the $(S_1/S_0)_{CI}$ and relaxes back to the S_0 surface upon which NO elimination takes place with no activation barrier.

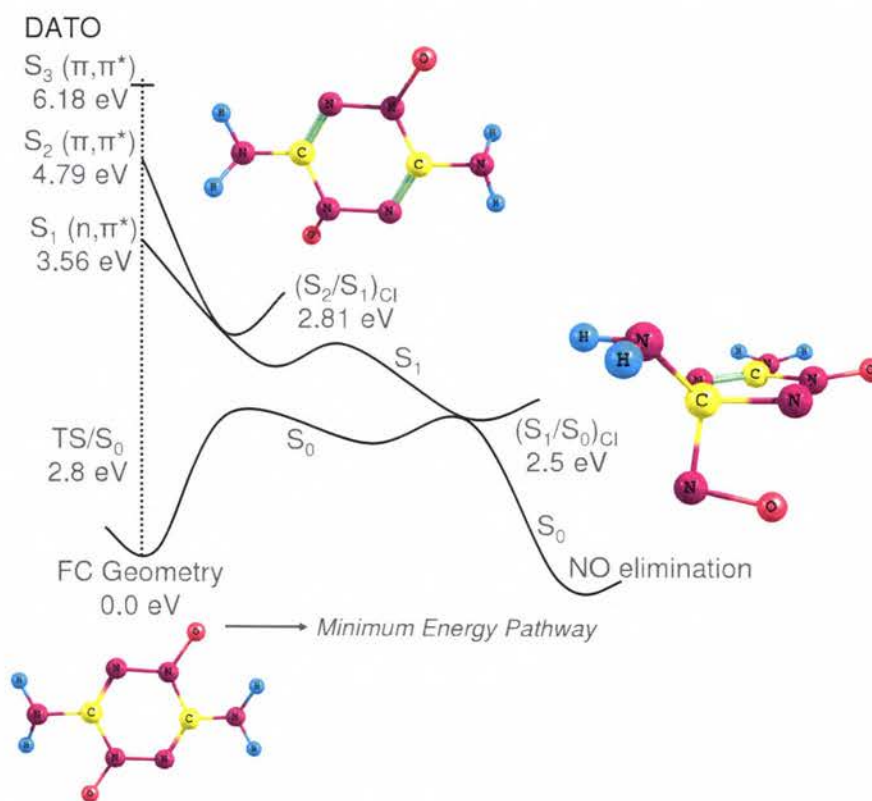


Figure 5.9: One dimensional projection of the multidimensional singlet electronic potential energy surfaces of DATO computed at CASSCF(10,8)/6-31G(d) level of theory. Geometry near the $(S_1/S_0)_{CI}$ supports a ring contraction mechanism for excited electronic state decomposition of DATO, which finally results in NO elimination. Note that ring contracted form of DATO near the $(S_1/S_0)_{CI}$ has a bent C-NO moiety attached to the triazole ring, which can finally generate a rotationally hot NO product.

5.6 Discussion

NO product is observed from all the tetrazine-N-oxide based molecules studied in the present work. The NO product from DAATO_{3,5} and ACTO displays similar cold rotational (20 K) and hot vibrational distributions (1200 K). DATO, on the other hand, renders hotter (50 K) rotational and colder (only (0-0) transition of NO is observed) vibrational distributions for the NO product. DAATO_{3,5} and ACTO differ from DATO primarily by the relative position of oxygen atoms attached to the tetrazine ring. Thus, we propose that the relative position of oxygen atoms in tetrazine-N-oxides will have significant effect on their energetic behavior: one of these O-N attachments could presumably be superior to the other with regard to the overall energetic properties of these systems.

Comparison of the rotational and vibrational distributions of the NO product from excited electronic state decomposition of N₂O to those of DAATO_{3,5}, ACTO, and DATO suggests that N₂O could not be an intermediate precursor for the NO product observed in the experiment. These results preclude an N₂O elimination pathway involved in the excited electronic state decomposition of tetrazine-N-oxide based molecules. Furthermore, this comparison shows that the excited electronic state decomposition of tetrazine-N-oxides evolves through a different mechanism than that of bare tetrazines, which are shown to decompose through a concerted triple dissociation mechanism leading to N₂ elimination.¹⁴ An N₂ product, however, can be generated from tetrazine-N-oxides through Meisenheimer rearrangement (see Figure 5.3). Currently, we have started (2+1) REMPI experiments at 203 nm for the detection of N₂ from these nitrogen rich molecules.²⁴

The theoretical results show that a ring contraction mechanism is involved in generation of an NO product from excited electronic state decomposition of ACTO and DATO. Ring contraction takes place near the $(S_1/S_0)_{CI}$ conical intersection as these molecules evolve from low lying excited electronic states.

Past studies on energetic materials have firmly established that conical intersections (due to breakdown of the Born-Oppenheimer approximation leading to the crossing of two adiabatic Born-Oppenheimer surfaces) are central features in the excited electronic state decomposition of energetic molecules.^{18,19} Decomposition dynamics of energetic materials are purely nonadiabatic in nature. One of the most important implications of a conical intersection is rapid and efficient internal conversion from upper to lower electronic state surfaces through radiationless transition.²⁵ This internal conversion facilitates rapid conversion of electronic energy (produced from an initiation pulse), belonging to the upper electronic state, to vibrational energy of the lower electronic state, with a potential time scale of a few femtoseconds. Therefore, the presence of conical intersections for the ring contraction reaction pathway of tetrazine-N-oxides suggests that initial NO elimination in the excited electronic state decomposition of tetrazine-N-oxides is ultrafast.

As mentioned above, the major structural difference between ACTO and DATO is the relative position of oxygen atoms attached to the tetrazine ring (2,4 vs. 1,4). Although a ring contracted geometry is optimized for both ACTO and DATO near the $(S_1/S_0)_{CI}$ conical intersection, one can notice a subtle difference in the geometry between ACTO and DATO, which can well explain the different energy distributions for the NO products from these two molecules. As shown in Figures 5.8 and 5.9, the C-

NO moiety attached to the five membered triazole ring is nearly linear ($\angle\text{CNO} \sim 150^\circ$) for ACTO, but is clearly bent ($\angle\text{CNO} \sim 95^\circ$) for DATO. The nearly linear C-NO moiety attached to the ring contracted form of ACTO near $(S_1/S_0)_{\text{CI}}$ probably exerts less torque on the terminal NO moiety than does the ring contracted form of DATO during the NO elimination process. This explains the observation of a rotationally cold (20 K) product for excited electronic state decomposition of ACTO. A bent C-NO moiety, on the other hand, attached to the ring contracted form of DATO near $(S_1/S_0)_{\text{CI}}$ can exert considerable torque on the terminal NO moiety during the NO elimination process. This $(S_1/S_0)_{\text{CI}}$ geometry difference explains the observation of rotationally hotter (50 K) distributions of the NO product from DATO.

Theoretical prediction for $\text{DAATO}_{3.5}$ is not possible at the CASSCF level of theory with a balanced active space; however, similar rovibrational spectral structures for the NO product observed in the experiment for both $\text{DAATO}_{3.5}$ and ACTO indicate that decomposition of $\text{DAATO}_{3.5}$ evolves through a similar ring contraction mechanism.

5.7 Conclusions

Present work on the unimolecular decomposition of tetrazine-N-oxide based high nitrogen content energetic molecules from their excited electronic states leads to a number of conclusions. Nitric oxide (NO) is observed to be an initial decomposition product from $\text{DAATO}_{3.5}$, ACTO, and DATO. Excited electronic state decomposition of $\text{DAATO}_{3.5}$, and ACTO produces a vibrationally hotter ($T_{\text{vib}} \sim 1200$ K), but rotationally colder ($T_{\text{rot}} \sim 20$ K) fragment NO product compared to that from DATO, which generates a vibrationally colder (only (0-0) transition of NO is observed), but

rotationally hotter ($T_{\text{rot}} \sim 50$ K) NO product. The relative positions of the oxygen atoms attached to the ring have significant effect on the final energy distribution among product molecules following decomposition of tetrazine-N-oxide based molecules. Decomposition behavior of N-oxides of tetrazine based molecules is different from that of the unsubstituted tetrazine molecule, and N_2O is not an intermediate precursor of the NO product. Theoretical calculation shows that an $(S_1/S_0)_{\text{CI}}$ conical intersection is involved in the excited electronic state decomposition of N-oxide based energetic molecules and that the NO product is generated through a ring contraction mechanism.

The cold vibrational distribution of the NO product from DATO decomposition reaction suggests that DATO would be a better energetic material than ACTO or $\text{DAATO}_{3.5}$ because potentially more energy can be partitioned in translational degrees of freedom for the products. This, of course, would depend to some extent on how the additional vibrational energy is distributed amongst all the decomposition products of the energetic material. Furthermore, these high nitrogen content energetic materials decompose from the excited electronic states in a fashion similar to that found for nitramine energetic materials; that is, through series of conical intersections to their ground electronic states. All these energetic molecules then decompose to yield NO from their highly vibrationally excited S_0 states.

5.8 Acknowledgments

Dr. David E. Chavez (LANL) is gratefully thanked for supplying samples of these and many other energetic materials and their model compounds, and the US ARO is gratefully acknowledged for support of this work.

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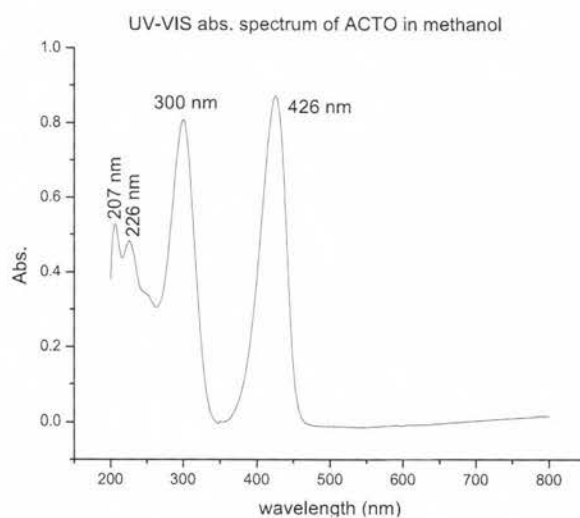
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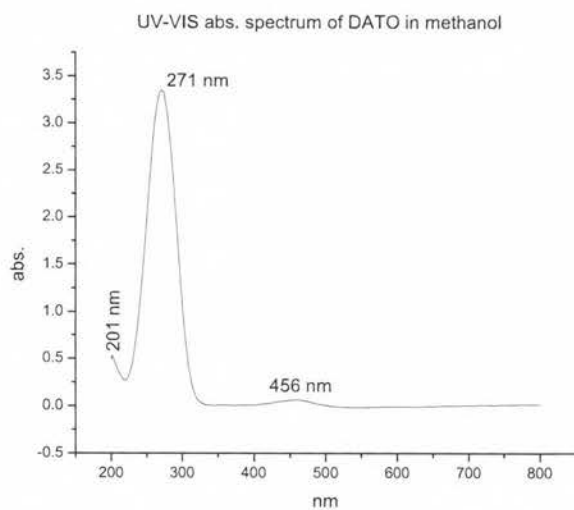
Supplementary Information

Figure 5.S1: UV-VIS absorption spectra of ACTO (a) and DATO (b) in methanol.

(a)



(b)



CHAPTER 6

Nonadiabatic Molecular Chemistry of Energetic Materials

Work presented in this chapter will be published as an invited article in “Bhattacharya, A.; Guo, Y. Q.; Bernstein, E. R. *Acc. Chem. Res.* **2010**.” Yuanqing and I worked together on the experiments and I worked independently on the theoretical calculations. Previous graduate student Hong Sun worked on the decomposition of RDX.

6.1 Introduction

Contemporary advances in chemical dynamics have witnessed that conical intersections (CIs), which arise due to the crossing of multidimensional electronic potential energy surfaces (PESs), play an important role in the processes involving excited electronic states of organic polyatomic molecules.¹ At these intersections the Born-Oppenheimer approximation breaks down, and interesting dynamical processes result, which can be observed spectroscopically. The particular topology of a conical intersection, which is often termed a ‘photochemical funnel’, provide an extremely fast (typically occurring on a characteristic timescale of femtoseconds) and highly efficient pathway for radiationless decay from upper to lower electronic states. Thus CIs enable

efficient electronically nonadiabatic chemistry (a process that spans multiple electronic PESs) to occur.^{1(c)}

Excited electronic states play a key role in the initial step of decomposition of energetic materials. They are easily generated by shock or compression waves.² Energetic materials are controllable storage systems of usable chemical energy, which have a number of industrial, civil, and military applications. Electronic excitation as the first molecular response in solid explosives under shock or compression waves is proposed to occur through several accepted mechanisms, including decreased HOMO-LUMO energy gap,^{2(e),2(f)} promotion of lattice defects,^{2(g)} shearing of crystal plates, and initiation of hole migration across the crystal. Undoubtedly, the specific topology of the excited electronic PESs of energetic materials will determine and control the decomposition of these materials following electronic excitation. Therefore, nonadiabatic chemistry of these materials through CIs is expected to play an important role in the initial step of their decomposition. While nonadiabatic chemistry through CI has been characterized and understood for a variety of chemical systems thus far,^{1(c)} its role in the initial step of decomposition of energetic materials has never been considered and judged before.³⁻⁶ Details of nonadiabatic chemistry through CIs in the initial steps of the decomposition of these materials must be recognized and understood to maximize release of the stored chemical energy in the most efficient and useful manner from these materials, and to understand completely their combustion chemistry. The process of understanding must begin with an exploration of their unimolecular behavior because such detailed information at the microscopic level may be used directly or as an input for molecular dynamics simulations to gain insight into the

condensed phase processes. Furthermore, if certain key unimolecular nonadiabatic steps can be identified, one can in principle make a material less or more sensitive or “energetic” by chemical modifications that raise or lower the activation energy barriers for these steps.

This chapter describes recent advances made in our understanding of nonadiabatic unimolecular chemistry of energetic species through CIs following electronic excitation. Here we highlight a number of new observations, some results from previous chapters, and a few works that have appeared recently in literature.⁹ The primary energetic systems, whose nonadiabatic chemistry is discussed here, are the nitro, nitramine, furazan, and tetrazine-N-oxide based energetic species.

6.2 Methodologies

A synergism between experiment and theory is absolutely necessary to provide a coherent description of nonadiabatic chemistry of energetic molecules at the molecular level because the presence of a CI in the reaction pathway can only be inferred from experimental data: confirmation requires a theoretical study of the relevant potential energy surfaces.

Decomposition of energetic materials is an extremely fast and complex process in which numerous chemical and physical events occur in a concerted or step-wise fashion. These reaction mechanisms are strongly dependent on a wide variety of factors. Determination of the mechanisms and dynamics of the dominant decomposition reaction of energetic materials and study of its nonadiabatic chemistry poses considerable challenges. Because of these difficulties, in the present approach, a model system is first studied in detail. A model system is typically a simple analogue molecule

with a single energetic moiety of a particular class of energetic material. It possesses both structural and electronic properties similar to the larger, more complex energetic material, but is more amenable to detailed experimental and theoretical studies than are the actual energetic species. For example, dimethylnitramine ((CH₃)₂NNO₂) is chosen as model system of nitramine energetic materials such as RDX, HMX and CL-20. Subsequently, nonadiabatic chemistry of energetic materials are studied and compared with that of the chosen model system to gain insight about decomposition of true energetic materials.

Experimental

Energy resolved and time resolved spectroscopic techniques are used to explore the decomposition mechanisms and dynamics of energetic molecules. The forces or torques that act on the departing fragments during dissociation of a parent molecule give rise to clear and characteristic patterns in the product internal state (rotational and vibrational) distributions. The internal energy/state distributions of the products generated following electronic excitation of the parent molecules are probed using mass and energy resolved spectroscopic techniques. Knowledge of internal energy distributions of the product molecules ultimately leads one to propose the decomposition mechanism of the energetic material. Subsequently, dynamics of the decomposition reaction is determined by femtosecond pump-probe spectroscopy. Details of the experimental methodologies utilizing time of flight mass spectrometry (TOFMS), laser induced fluorescence (LIF) spectroscopy, resonance enhanced multiphoton dissociation schemes, ns dye laser, and fs laser systems can be found in the previous chapters.

Theoretical

From a theoretical point of view, multiconfigurational methodologies (such as, CASSCF, CASMP2) are used to explore nonadiabatic molecular processes in excited electronic state chemistry of energetic molecules to model experimental observations. Geometries at the lowest energy CIs are optimized using the complete active space self consistent field (CASSCF) methodology. Relevant reaction paths are computed to obtain mechanistic insights concerning nonadiabatic processes of energetic systems. Details of the theoretical procedures utilizing Gaussian 03 quantum mechanical software can be found in previous chapters. Selection of active space in a CASSCF computation is an important, which is elaborately discussed in Appendix IV and VI in this thesis.

6.3 Nonadiabatic Chemistry of Nitramines (N-NO₂)

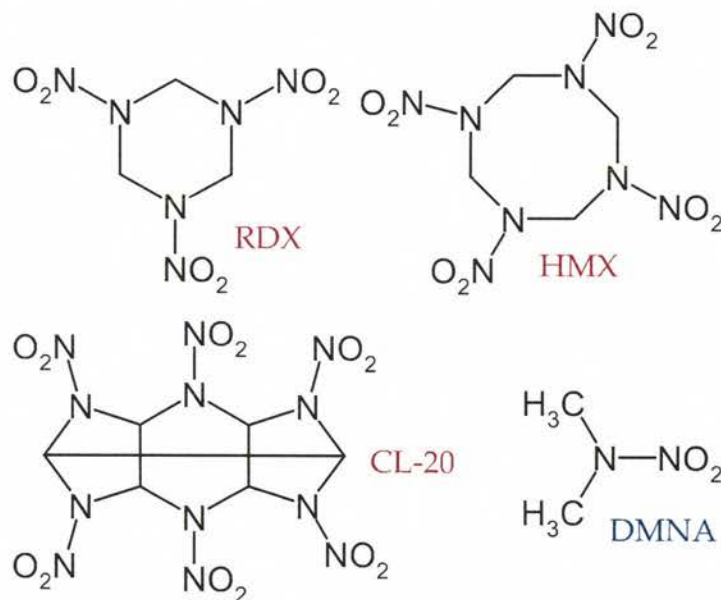


Figure 6.1: Chemical structures of nitramine energetic materials RDX, HMX, and CL-20 and nitramine model system dimethylnitramine (DMNA).

Nitramine energetic materials, such as RDX (1,3,5-trinitro-1,3,5-triazacyclohexane), HMX (1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane), and CL-20 (2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane) have broad application as explosives and fuels due to their high energy content. These materials have different numbers of N-NO₂ (nitramine) energetic moieties, as shown in Fig. 6.1. In the effort to explore the nonadiabatic chemistry of nitramine energetic molecules, different excited electronic state processes of a model system with a single N-NO₂ energetic moiety, dimethylnitramine (DMNA, (CH₃)₂NNO₂) are first discussed in detail.³ Subsequently, nonadiabatic chemistry of larger and more complex nitramine energetic materials are addressed and compared with that of DMNA.

DMNA. Nitric oxide (NO) is observed as a major decomposition product from dissociation of DMNA at 226 nm electronic excitation in TOFMS and LIF spectroscopy through the resonance (0-0) vibronic band of the [$A^2\Sigma \leftarrow X^2\Pi$] electronic transition of NO. In addition, LIF spectroscopy detects hydroxy (OH) radical from decomposition of DMNA at 226 nm using (0-0) vibronic band of [$A^2\Sigma \leftarrow X^2\Pi$] electronic transition of OH at 308 nm. Comparing maximum LIF signal intensities of NO and OH radicals along with their respective Franck-Condon factors for the (0-0) transition and the population of rotational states responsible for the transition, the yield ratio between the NO and OH products is calculated to be 1:0.04. This ratio indicates that 96% of the total excited electronic state decomposition of DMNA occurs through the NO elimination channel and the remaining 4% of the total decomposition of DMAN occurs through OH elimination.

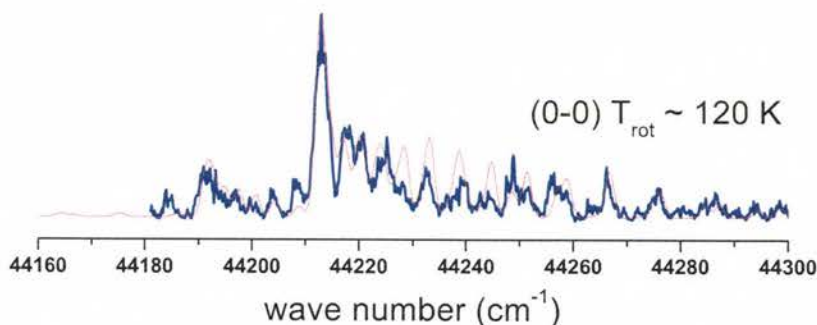


Figure 6.2: One color (1+1) R2PI spectra of the vibronic transitions [$A^2\Sigma^+$ ($v'=0$) $\leftarrow$ $X^2\Pi$ ($v''=0$)] of the NO product from the excited electronic state decomposition of DMNA. Rotational temperature simulations with Boltzmann distribution show that NO from DMNA generates rotational temperatures of 120 K.

The internal (rotational and vibrational) energy state distributions of the products NO and OH are estimated from their energy resolved spectra. The (1+1) R2PI spectrum of NO from photolysis of DMNA in the NO $A^2\Sigma$ ($v'=0$) $\leftarrow$ $X^2\Pi$ ($v''=0$) transition region is presented in Figure 6.2. Comparison of the simulated spectrum based on a Boltzmann population distribution for the NO rotational energy levels at the $v''=0$ state to the R2PI spectrum of the NO product from DMNA generates a hot rotational temperature of 120 K. A similar rotational temperature for the NO product is also obtained from LIF spectroscopy. The LIF spectrum of OH (shown in Figure 6.3) from photolysis of DMNA at 226 nm shows a very hot rotational distributions with a rotational temperature of 1500 K. Thus both NO and OH products from decomposition of DMNA following electronic excitation at 226 nm are generated rotationally hot. This experimental observation clearly infers that a torque acts on the departing NO or OH moiety during dissociation of the parent molecule, resulting in rotationally hot products.

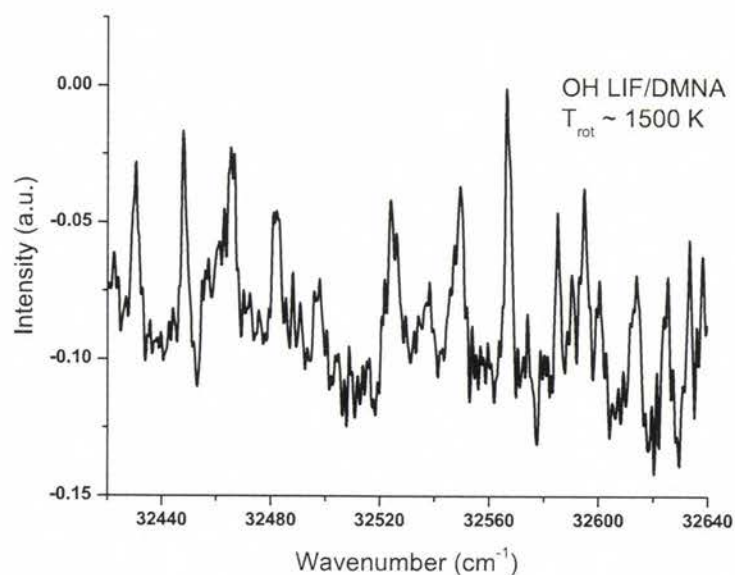


Figure 6.3: LIF spectrum of OH near 308 nm from excited electronic state decomposition of DMNA at 226 nm.

Observation of an OH LIF signal following decomposition of DMNA at 226 nm photoexcitation corroborates the fact that HONO elimination channel is involved in the decomposition of DMNA. The large discrepancy between the OH and NO yields observed in LIF experiments indicates that the HONO elimination channel has only a minor contribution to the overall excited electronic state decomposition of DMNA. In fact, 4% branching ratio for the HONO elimination channel is estimated from experimentally observed yield of OH, which is in good agreement with that of 3% reported in previous work.⁷

Photolysis of DMNA at 226 and 193 nm is also performed inside a quartz capillary attached to the pulsed nozzle, and subsequent products are detected by 118 nm ionization in TOFMS. Electronic excitation of DMNA at both 226 and 193 nm renders a fragment signal corresponding to $(\text{CH}_3)_2\text{NOH}$ at mass channel 61 amu. This fragment

signal can only be generated through a nitro-nitrite isomerization pathway. Therefore, the initial NO product produced following excited electronic state decomposition of DMNA at 226 nm arises through nitro-nitrite isomerization mechanism.



Thus, experimental results suggest that 96% of total decomposition of DMNA occurs through a nitro-nitrite isomerization and 4% of the total decomposition of DMNA happens through HONO elimination.

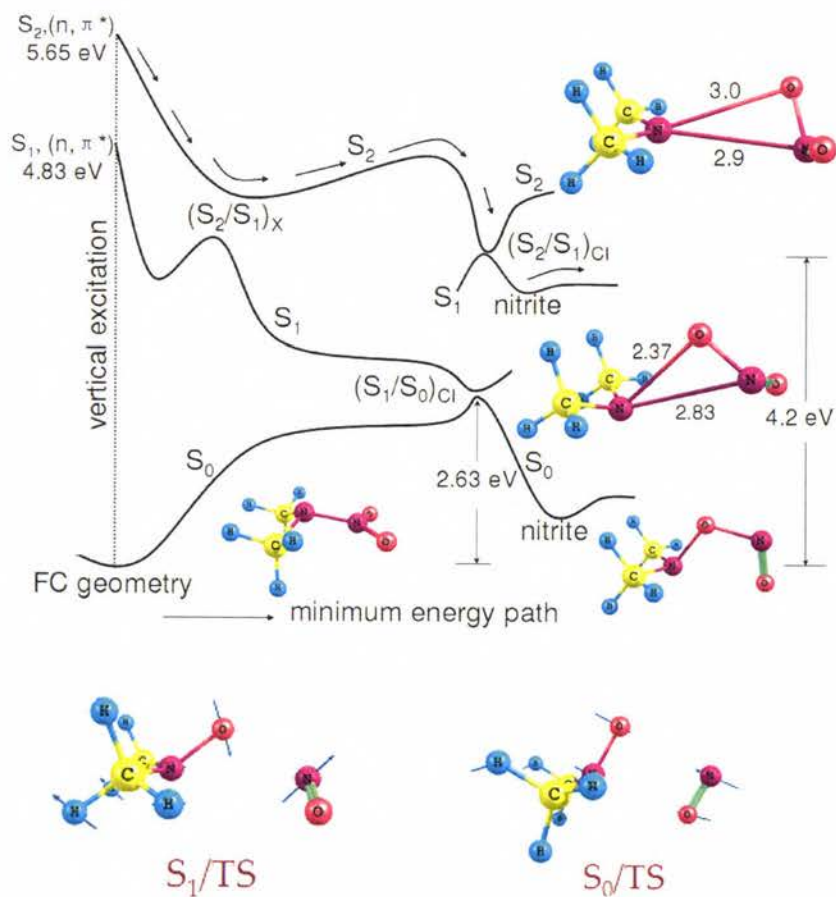


Figure 6.4: One dimensional projection of the multidimensional electronic potential energy surfaces of DMNA computed at the CASSCF(10,7)/6-31G(d) level of theory. Path arrows represent the classical trajectory of the plausible excited electronic state decomposition mechanism of DMNA. NO elimination TSs are shown at the bottom.

Theoretical calculations using a CASSCF(10,7)/6-31G(d) level of theory shows that electronically excited state potential energy surfaces of DMNA are highly coupled along this reaction coordinate, allowing nonadiabatic chemistry to occur through this pathway. A schematic one-dimensional projection of the multidimensional singlet potential energy surfaces (S_0 , S_1 , and S_2 calculated at CAS(10,7)/6-31G(d)) of DMNA with location and structures of different conical intersections is plotted in Figure 6.4. Path arrows in this figure indicate the classical trajectory of the possible decomposition pathway for the excited electronic state decomposition of DMNA at 226 nm.

Comparison of vertical excitation energies of different singlet excited electronic states ($S_1=4.83$ eV and $S_2=5.65$ eV) with experimental excitation energy (5.5 eV at 226 nm) infers that irradiation of isolated molecular DMNA at 226 nm populates the S_2 excited electronic state. As can be seen in Figure 6.4, vertical excitation to the FC point of the S_2 state can potentially lead to the nonadiabatic nitro-nitrite isomerization through $(S_2/S_1)_{CI}$. On the S_1 surface the nitrite form dissociates through an NO elimination pathway. The unstable normal mode of vibration for the transition state associated with this NO elimination from nitrite on the S_1 surface shows a torque which acts on the terminal NO moiety. Thus this NO elimination pathway following nitro-nitrite isomerization is expected to generate rotationally hot product NO. This theoretical conclusion is consistent with the experimental observation of a rotationally hot (120 K) NO product following decomposition of DMNA at 226 nm.

Another possible decomposition pathway from the FC point of the S_2 surface of DMNA begins with an initial internal conversion of the molecule to the S_1 surface through $(S_2/S_1)_X$. Then DMNA can be directed to the $(S_1/S_0)_{CI}$ conical intersection at

which point the molecule can undergo a nitro-nitrite isomerization. The nitrite form further decomposes through an NO elimination pathway on the ground state potential energy surface. This pathway, however, is considered to be less probable for two reasons.

(1) The rate of nonadiabatic transition through a conical intersection depends on the energy gap between the two adiabatic surfaces near conical intersection. A small adiabatic energy gap (nonadiabatic coupling term will dominate) enhances the probability (thus, rate) of nonadiabatic transition from the upper to the lower electronic state near the conical intersection. The computed energy gap between S_2 and S_1 adiabatic surfaces near $(S_2/S_1)_X$ and $(S_2/S_1)_{CI}$ are 487 cm^{-1} and 0.73 cm^{-1} , respectively, at the CASSCF(10,7)/6-31G(d) level of theory. Therefore, in a dynamical sense, the nonadiabatic transition through $(S_2/S_1)_{CI}$ will dominate over that through $(S_2/S_1)_X$. As a result, nitro-nitrite isomerization through the $(S_2/S_1)_{CI}$ conical intersection is expected to be the major decomposition channel of DMNA from FC point of S_2 surface.

(2) The unstable normal mode of vibration for the transition state associated with NO elimination from nitrite on the S_1 surface shows a finite torque which acts on the terminal NO moiety. Angular displacement for the unstable normal mode of vibration for NO elimination TS on the S_1 surface is shown in Figure 6.4. A similar transition state on the ground state surface does not show such significant torque on the terminal NO moiety. Rather, the unstable normal mode of vibration for NO elimination TS on the ground state surface shows parallel displacement for terminal NO moiety (see Figure 6.4). Therefore, the NO product should be rotationally hot if NO elimination occurs on the S_1 surface following nitro-nitrite isomerization through $(S_2/S_1)_{CI}$, and the

NO product should be rotationally cold if NO elimination occurs on the S_0 surface following nitro-nitrite isomerization through $(S_1/S_0)_{CI}$. As the NO product is observed experimentally to be rotationally hot (120 K), nitro-nitrite isomerization through $(S_2/S_1)_{CI}$ is the appropriate and probable pathway because it can produce rotationally hot NO product.

Following nonadiabatic transition from S_2 to S_1 state through the $(S_2/S_1)_{CI}$, DMNA, in principle, can undergo either nitro-nitrite isomerization or NO_2 elimination on the S_1 surface. The isomerization channel on the S_1 surface following $(S_2/S_1)_{CI}$, however, is calculated to be the minimum energy pathway (see Figure 6.5). A ~ 3 kcal/mol energy barrier exists for the NO_2 elimination pathway, but no energy barrier is found for the nitro-nitrite isomerization channel on the S_1 surface following $(S_2/S_1)_{CI}$.

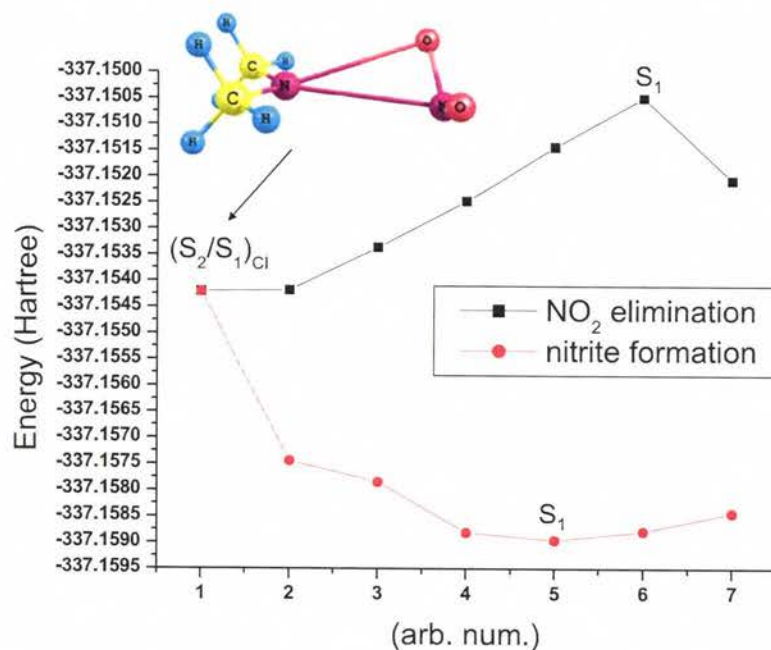


Figure 6.5: Potential energy surface scan of DMNA along N-NO_2 bond elongation (square) and N-ONO bond formation (circle) reaction coordinates from $(S_2/S_1)_{CI}$ conical intersection following S_1 gradient vector at CASSCF(10,7)/4-31G level of theory.

Thus, following electronic excitation of DMNA to its S_2 surface, nitro-nitrite isomerization takes place near the $(S_2/S_1)_{CI}$ CI. This isomerization occurs through a loose geometry in which the NO_2 moiety interacts with the $(CH_3)_2N$ moiety from a considerably long distance (~ 2.8 Å) through a relatively weak interaction (~ 3 kcal/mol). If enough vibrational energy is provided to the intermolecular modes of these two moieties during this excited state isomerization process, they can promptly diffuse away and can undergo NO_2 elimination. Therefore, experimental condition can influence the nonadiabatic chemistry of DMNA.

At room temperature, molecules are thermally hot (~ 300 K). Therefore, hot parent molecules can provide enough vibrational energy to the intermolecular modes of DMNA that the NO_2 and $(CH_3)_2N$ moieties can diffuse away in spite of their initial close proximity during isomerization, resulting in NO_2 elimination as the major decomposition channel. This is the reason why decomposition of DMNA, at 248 nm and 266 nm photoexcitations at room temperature under almost collisionless conditions, was observed to occur through NO_2 elimination.⁷ In the molecular beam, however, molecules are extraordinarily cold (~ 1 K) and thus the two moieties NO_2 and $(CH_3)_2N$ can remain in close proximity, rendering nitro-nitrite isomerization as the major decomposition channel. The same is possible even at room temperature in a dense gaseous medium, for which cage effects can again keep the two moieties in the close proximity, resulting in nitro-nitrite isomerization as a major decomposition channel. Both have been observed in our experiments. Thus, nonadiabatic chemistry controls the decomposition mechanism of DMNA following electronic excitation: a low lying

conical intersection provides a direct pathway for excited electronic state decomposition of DMNA from its S_2 state through a nitro-nitrite isomerization.

RDX, HMX, and CL-20. Nitro-nitrite isomerization is observed to be the only excited electronic state decomposition channel for large and more complex nitramine energetic materials such as RDX, HMX, and CL-20.⁸ NO is generated through this mechanism as an initial decomposition product from all three of these energetic molecules. The (1+1) R2PI spectra of NO from photolysis of RDX in the NO $A^2\Sigma^+ (v'=0) \leftarrow X^2\Pi (v''=0,1,2,3)$ transition region are presented in Figure 6.6. Comparison of simulated spectra based on Boltzmann population distributions of the NO rotational energy levels at the $v''=0,1,2,3$ states to the R2PI spectra of the NO product from RDX generates a cold rotational temperature of 20 K and a hot vibrational temperature of 1800 K.

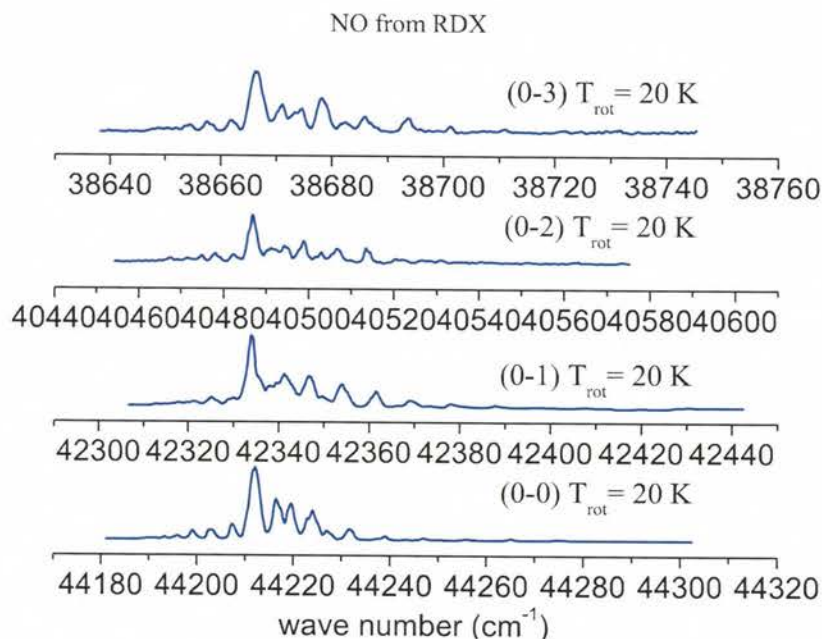


Figure 6.6: One color (1+1) R2PI spectra of the vibronic transitions [$A^2\Sigma^+ (v'=0) \leftarrow X^2\Pi (v''=0,1,2,3)$] of the NO product from the excited electronic state decomposition of RDX. Rotational and vibrational temperature simulations with Boltzmann distribution show that NO from RDX generates rotational and vibrational temperatures of 20 K and 1800 K, respectively.

Similar distributions of the product NO are also observed from excited electronic state decomposition of HMX and CL-20. The ratio of TOFM signal intensity of NO generated from RDX, HMX, and CL-20 is estimated to be 3:4:6, which correspond to the number of nitramine moieties in each molecule, respectively. This result indicates that energetic materials decompose via the same mechanism through which each nitramine group yields an NO molecule. Furthermore, vibrationally very hot (~ 1800 K) distribution of the NO product generated from decomposition of RDX, HMX, and CL-20 suggests that nitramine energetic materials dissociate on their ground potential energy surface following a rapid internal conversion from upper excited electronic state to the ground state. This internal conversion transfers the electronic excitation energy to the vibrational energy. The excess vibrational energy stored in the molecule subsequently helps dissociate the chemical bonds of RDX, HMX, and CL-20 through nitro-nitrite isomerization pathway. Thus decomposition of RDX, HMX, and CL-20 is necessarily nonadiabatic, and an $(S_1/S_0)_{CI}$ should be involved in nitro-nitrite isomerization processes.

For theoretical exploration of nonadiabatic decomposition behavior of RDX, HMX, and CL-20, search of the lowest energy conical intersection along nitro-nitrite isomerization reaction coordinate needs to be conducted. This search, however, is not possible using computationally more expensive CASSCF methodology for RDX, HMX, and CL-20 because this level of theory requires very large (more than 40 active orbitals including all nonbonding $n\sigma_O$, π , and bonding and antibonding σ_{NN} and σ_{NO}) active space for these molecules. Present computational facilities using Gaussian or

Molpro can not accommodate CASSCF calculations using such a large active space. Reduction of active space does not solve the problem; rather it introduces spurious effects in the computational results. Due to this reason, recently less expensive time dependent density functional theory (TDDFT) or configuration interaction with single excitations (CIS) calculations are employed to find out vertical excitation energies of RDX. Appropriateness of these levels of theory to explore excited electronic state potential energy surfaces of RDX, however, is questionable. Therefore, theoretical exploration of nonadiabatic chemistry of large and more complex nitramine energetic molecules, such as RDX, HMX, and CL-20, still poses challenge to the present computational capabilities.

Discussion. In spite of our inability to explore excited electronic state potential energy surfaces of nitramine energetic materials accurately, comparison of excited electronic state decomposition of energetic materials with that of their model systems provides a number of important insights regarding the nonadiabatic chemistry of energetic materials. The NO product generated from decomposition of RDX, HMX, and CL-20 is observed to be rotationally cold (20 K) following electronic excitation at 226, 236, 248, and 254 nm. This result infers that these materials have a single dissociation channel producing only a rotationally cold (20 K) distribution of the product. Therefore, excited electronic states of these materials are highly dissociative in nature so that all the UV electronic excitation energies used in the experiment yields similar rotational distributions of the NO product through the same pathway. Electronic excitation at different excitation energy does not change the decomposition pathway. This decomposition occurs on the ground electronic state surface following an internal

conversion from the upper to the lower electronic state through an $(S_1/S_0)_{CI}$ in the nitro-nitrite isomerization reaction coordinate. This generates a vibrationally very hot NO product.

Model systems such as DMNA, on the other hand, dissociate on the excited electronic state following internal conversion from the S_2 to the S_1 state through $(S_2/S_1)_{CI}$. Nitro-nitrite isomerization occurs through this nonadiabatic pathway, generating vibrationally cold but rotationally hot distributions of the NO product. From this comparison between the decomposition of energetic materials and their model systems, one necessarily concludes that unimolecular excited electronic state decomposition of a nitramine energetic system is dominated by its nonadiabatic behavior. Presence of a CI in the nitro-nitrite isomerization reaction coordinate provides a direct pathway for successful excited electronic state chemistry. Therefore, in order to predict molecular explosive behavior of nitramine energetic materials, knowledge of their nonadiabatic chemistry is of paramount importance. To determine the outcome of their unimolecular reactions, consideration of dynamics through the relevant and appropriate CI in the nitro-nitrite isomerization reaction coordinate is also important.

Conclusions. Electronic excitation of DMNA to S_2 state promotes an electron from an $n\sigma_O$ to π^* orbital; this electronic excitation initiates nitro-nitrite isomerization through $(S_2/S_1)_{CI}$. The nitrite subsequently dissociates on the S_1 surface, generating rotationally hot (120 K) NO product through the NO elimination pathway. Electronic excitation of RDX, HMX, and CL-20 also produces NO as initial decomposition product; however, the decomposition occurs on the ground potential energy surface following rapid

internal conversion to the ground state. Thus, excited electronic state processes of nitramine energetic molecules are highly nonadiabatic. Dynamics through conical intersections in the nitro-nitrite reaction coordinate determines their unimolecular decomposition.

6.4 Comparison of the Nonadiabatic Chemistry of nitromethane (C-NO₂) and dimethylnitramine (N-NO₂)

Nitro-containing energetic materials are frequently used as military explosives, propellants, and fuels. The nitro functional group in these compounds is often found to be bonded to carbon or nitrogen. In spite of possessing the same NO₂ functional group in all the nitro-containing energetic materials, different X-NO₂ (X=C,N) bond connectivities for the C-NO₂ (nitroalkane) and N-NO₂ (nitramine) energetic moieties makes them unique and different from each other. With regard to sensitivity, in general, nitramines are more sensitive to shock or impact than are nitroalkanes. The simplest analogue molecules with different X-NO₂ (X=C,N) energetic moieties are nitromethane with a C-NO₂ moiety and dimethylnitramine (DMNA) with an N-NO₂ moiety. To gain insight into the differences in nonadiabatic reactivity of nitromethane and DMNA, excited electronic state decomposition of these two molecules are compared and contrasted below. We shall see how different nonadiabatic chemistry determines the decomposition products for C-NO₂ and N-NO₂ containing compounds.

CH₃NO₂. The fragmentation products following electronic excitation of NM at 193 nm photoexcitation are observed to be CH₃ and electronically excited NO₂ (1²B₂). Florescence emission from 1²B₂ state of NO₂ with a long life-time (4 μs) in the visible region is observed following photodissociation of NM at 193 nm. The NO₂ fragment in the 1²B₂ excited state can dissociate into NO (X) and O as secondary products.

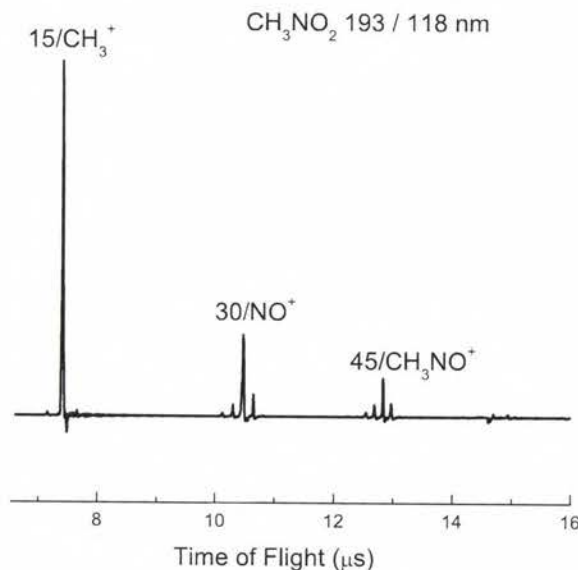


Figure 6.7: Mass spectrum of the photodissociation of nitromethane following excitation at 193 nm. A nanosecond 118 nm laser pulse is employed to ionize the dissociation products. CH₃, NO and CH₃NO are apparent product peaks, small peaks around NO and CH₃NO are impurity signals from 193 nm ionization. Only 118 nm laser does not produce any of these mass signals.

As illustrated in the mass spectrum (Figure 6.7) obtained by 118 nm ionization of products generated employing electronic excitation of nitromethane at 193 nm, the signal corresponding to CH₃ mass channel shows highest intensity. This confirms that C-NO₂ bond dissociation is the primary process for the dissociation of nitromethane following electronic excitation at 193 nm and that the NO₂ molecule should be the precursor for the NO product observed in TOFMS (Figure 6.7). Furthermore, a third product CH₃NO with mass of 45 amu shows that O atom elimination also occurs after the $\pi^* \leftarrow \pi$ excitation of nitromethane. Compared to the signal intensity of CH₃ and NO products, the CH₃NO product displays relatively weak intensity, which confirms that

the O atom elimination is a minor decomposition channel for nitromethane following the $\pi^* \leftarrow \pi$ excitation.

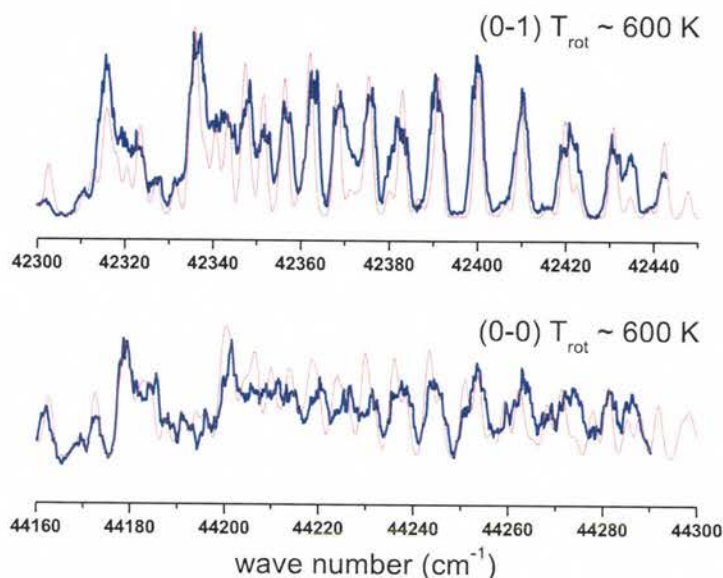


Figure 6.8: One color (1+1) R2PI spectra of the vibronic transitions of the NO product from excited electronic state decomposition of NM ($C-NO_2$). Rotational temperature simulations with Boltzmann distribution show that NO from NM generates rotational temperature ~ 600 K, whereas NO from DMNA renders rotational temperature ~ 120 K.

Both NO and CH_3 radicals are observed following decomposition of nitromethane at 226 nm. The NO product in its ground state is probed at 226 and 236 nm through its $A^2\Sigma (v'=0) \leftarrow X^2\Pi (v''=0,1)$ transition. The (1+1) R2PI spectrum of the NO product from photodissociation of nitromethane at 226 and 236 nm is shown in Figure 6.8. The spectra in the figure are rotationally resolved; most of the features originate from the $^2\Pi_{1/2}$ component of the ground electronic state of NO. Spectral simulation based on the Boltzmann population distribution produces a rotational temperature of 600 K for the NO product. One color (2+1) REMPI was also employed to probe CH_3 product from the photolysis of nitromethane at 226 nm. (2+1) REMPI

spectrum of CH_3 radical is presented in Figure 6.9, which shows a sharp Q-branch with no resolved rotational structure. Rotational temperature of CH_3 radical is calculated to be 200 K.

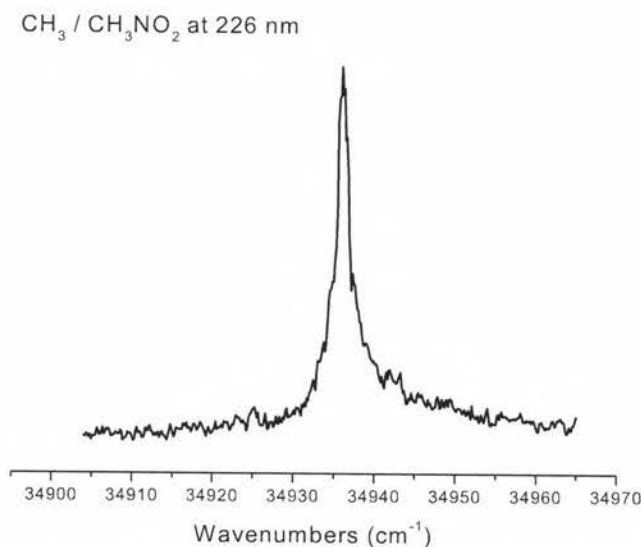


Figure 6.9: Two-color (286 and 118 nm), (2+1) REMPI of the CH_3 , following $[4p^2A'' \leftarrow X^2A']$ electronic transition, produced from photolysis of nitromethane at 226 nm

The TOFMS of the photodissociation of nitromethane under fs 226 nm radiation is presented in Figure 6.10, which shows mass signals corresponding to CH_3 , NO , and NO_2 . Direct observation of CH_3 and NO_2 fragments further confirms that C- NO_2 bond dissociation should be the primary processes for the photolysis of nitromethane.

Therefore, experimental results suggest that the major unimolecular decomposition channel of nitromethane following its $\pi^* \leftarrow \pi$ electronic excitation is C- NO_2 bond dissociation. The O-elimination channel has only a minor contribution to the overall decomposition of this molecule. Nitro-nitrite isomerization is not involved in the overall decomposition of nitromethane.

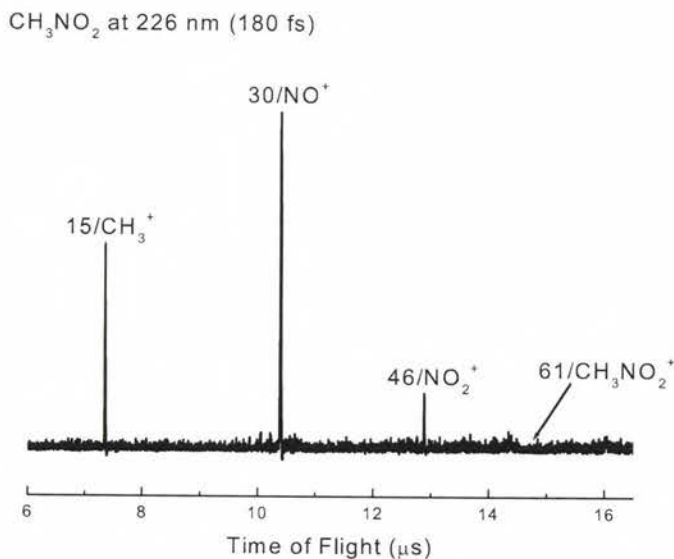


Figure 6.10: Mass spectrum of the photolysis of nitromethane at femtosecond 226 nm. The parent ion at mass channel 61 amu is not observed.

A theoretical model of the nonadiabatic chemistry of nitramine is given by Soto *et al.*¹⁰ at the CASPT2/ANO-L level of theory, which exactly fit the above experimental observations. The energy profiles running from the geometry of the FC point to different conical intersections are presented in Figure 6.11. The key mechanistic step in the photodissociation dynamics of nitromethane at 193/226 nm begin with the radiationless nonadiabatic internal conversion from S₃ to the S₂ surface through (S₃/S₂)_{CI}.

On the S₂ surface the following reaction pathways are accessible.

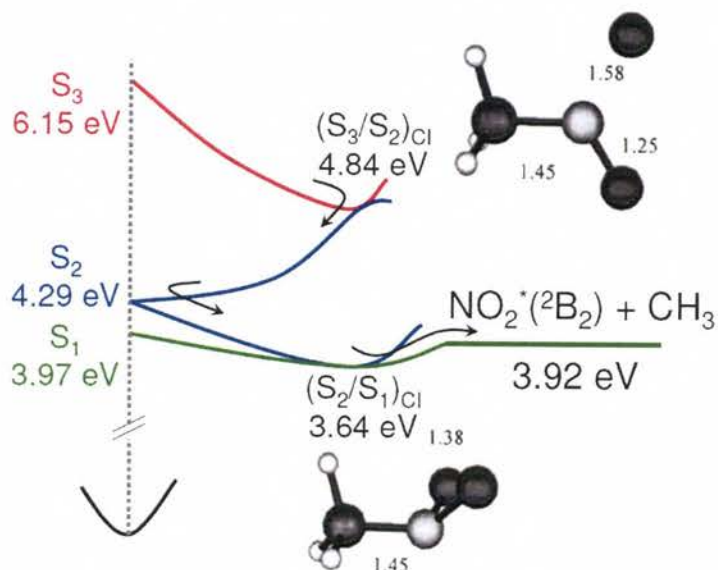


This reaction pathway, however, is not the minimum energy pathway (steepest decent pathway). Nonadiabatic transition from S₃ to S₂ state through (S₃/S₂)_{CI} should lead mostly to the minimum energy pathway which is further nonadiabatic deactivation to S₁ state through (S₂/S₁)_{CI}

On the S_1 surface, the molecule reaches C-NO₂ bond dissociation limit which is only 6 kcal/mol above the $(S_2/S_1)_{Cl}$.



A.



B.

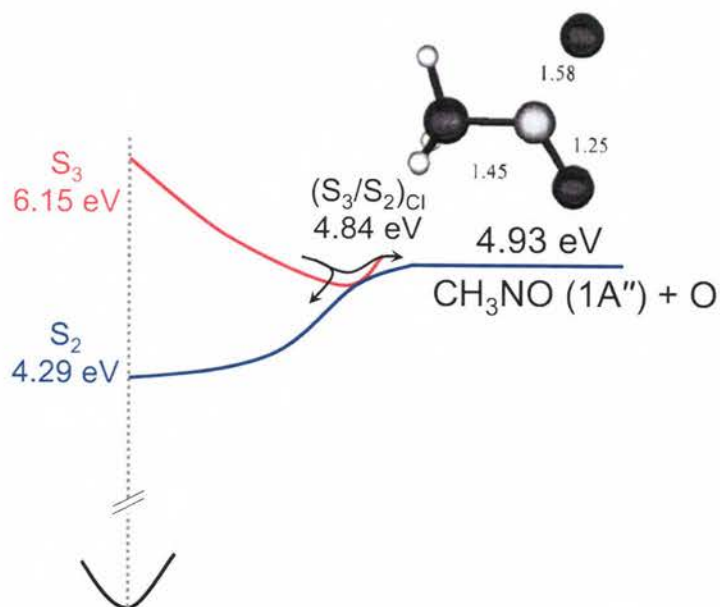


Figure 6.11: One dimensional projection of the multidimensional electronic potential energy surfaces of nitromethane computed at the CASPT2(14,11)/ANO-L level of theory. Two nonadiabatic reaction paths are explored: A. C-NO₂ bond dissociation, B. O-elimination. Path arrows represent the classical trajectory of the plausible excited electronic state decomposition mechanism of nitromethane.¹⁰

Discussion and Conclusions. The decomposition of nitromethane (with a C-NO₂ moiety) is mechanistically different from that of DMNA (with an N-NO₂ moiety) following their $\pi^* \leftarrow \pi$ electronic excitations. DMNA dissociates through a nitro-nitrite isomerization pathway; nitromethane dissociates through C-NO₂ bond dissociation pathway. Both pathways are electronically nonadiabatic; however, the nitro-nitrite isomerization of DMNA involves nonadiabatic transition through (S₂/S₁)_{CI} and the C-NO₂ bond dissociation pathway of nitromethane involves nonadiabatic transitions through (S₃/S₂) and (S₂/S₁)_{CI} CIs. No conical intersection is optimized in the nitro-nitrite isomerization reaction coordinate for nitromethane at CASSCF(14,11)/6-31G(d) level of theory. Therefore, specific topology of excited electronic state surfaces near conical intersections controls decomposition behavior of two different nitro-containing species: nitroalkanes (C-NO₂) and nitramines (N-NO₂). Their nonadiabatic chemistries are essentially different.

6.5 Nonadiabatic Chemistry of Furazans

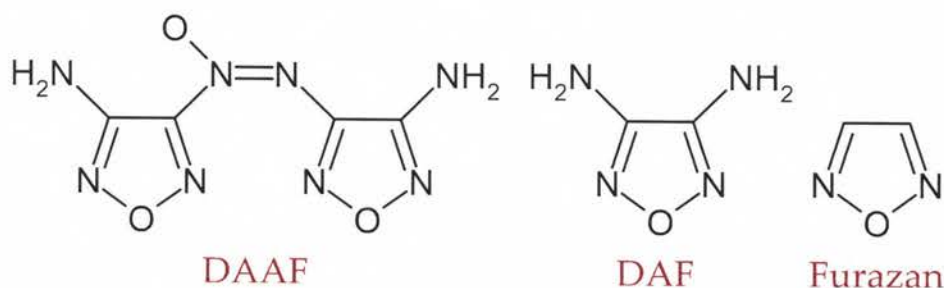


Figure 6.12: Chemical structure of furazan based molecules, DAAF, DAF and furazan.

Recently a series of furazan based high nitrogen content energetic materials, especially DAAF (3,3'-diamino-4,4'-azoxyfurazan), have received great attention due to their favorable properties: these include good heat resistivity, high heat of formation,

low sensitivity, and good detonation performance for applications as high explosives, fuels, and propellants. The structure (illustrated in Figure 6.12) of DAAF consists of two aromatic amino furazan rings connected by an azoxy group. For exploration of nonadiabatic chemistry of DAAF, two model systems are selected: DAF (diaminofurazan) and furazan. Their structures are illustrated in Figure 6.12. A systematic comparison of the excited electronic state decomposition mechanism for DAAF and its model systems (DAF and furazan) will generate detailed insight into, and understanding of, the initial nonadiabatic chemistry of furazan based energetic materials.

DAAF.

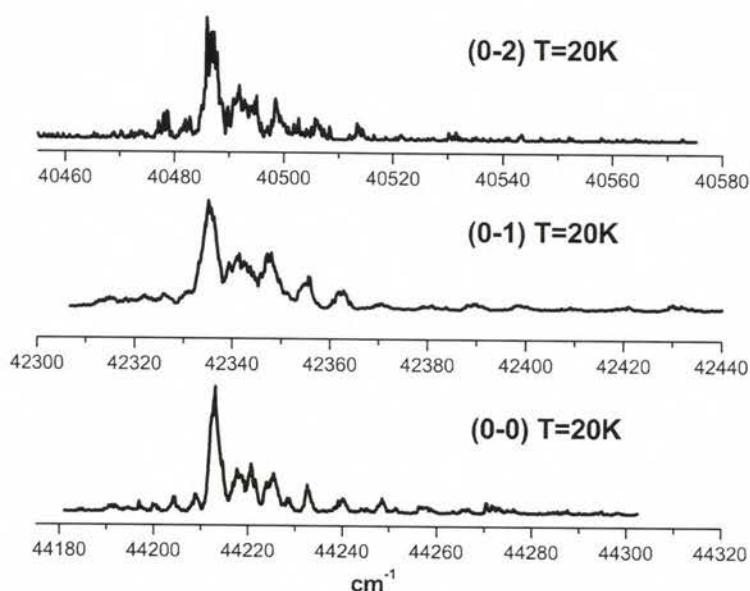


Figure 6.13: One-color (1+1) R2PI spectra of the vibronic transitions [$A^2\Sigma^+$ ($v'=0$) $\leftarrow$ $X^2\Pi$ ($v''=0,1,2$)] of the NO product from the excited electronic state decomposition of DAAF molecule. Rotational temperature simulations with Boltzmann distribution show that the three observed vibrational levels on the ground electronic states have a similar rotational temperature of 20 K.

NO is observed to be an initial decomposition product from photolysis of DAAF, DAF, and furazan. (1+1) R2PI spectra of the three vibronic transitions, $A^2\Sigma^+(v'=0)\leftarrow X^2\Pi(v''=0,1,2)$ of the NO molecule observed from decomposition of DAAF from its excited electronic state are shown in Figure 6.13. The three spectra in this figure have similar rotational structure but have a different absolute intensity for each vibronic band. Spectral simulation based on the Boltzmann population distributions for the three vibronic transitions of the NO product from DAAF produces similar rotational temperatures (~ 20 K) for three vibrational levels ($v''=0,1,2$) in the ground electronic state. The vibrational temperature of the NO product from DAAF can also be obtained by simulating the relative intensities among the observed vibronic bands using Boltzmann population distribution analysis. By comparing the experimental data with simulation at different vibrational temperatures, the vibrational temperature of the NO product from DAAF is estimated to be 1260 K. Thus, experimental results suggest that DAAF displays excitation wavelength independent dissociation channel because it generated only cold rotational distributions (20 K) of the NO product at all three excitation energies (5.49 eV, 5.26 eV, and 5.00 eV).

DAF and furazan. Similar (1+1) R2PI spectra of three vibronic transitions, $A^2\Sigma^+(v'=0)\leftarrow X^2\Pi(v''=0,1,2)$ of the NO molecule obtained from excited electronic state decomposition of DAF are shown in Figure 6.14. The (0-0), and (0-1) vibronic bands of the NO product from DAF show similar rotational patterns to those of the NO product from DAAF, and the rotational temperature of these two bands is also about 20 K. The (0-2) vibronic band of the NO product from DAF shows much hotter rotational

distribution than that of the (0-0) and (0-1) vibronic bands. Spectral simulation for the (0-2) band yields a rotational temperature of about 100 K.

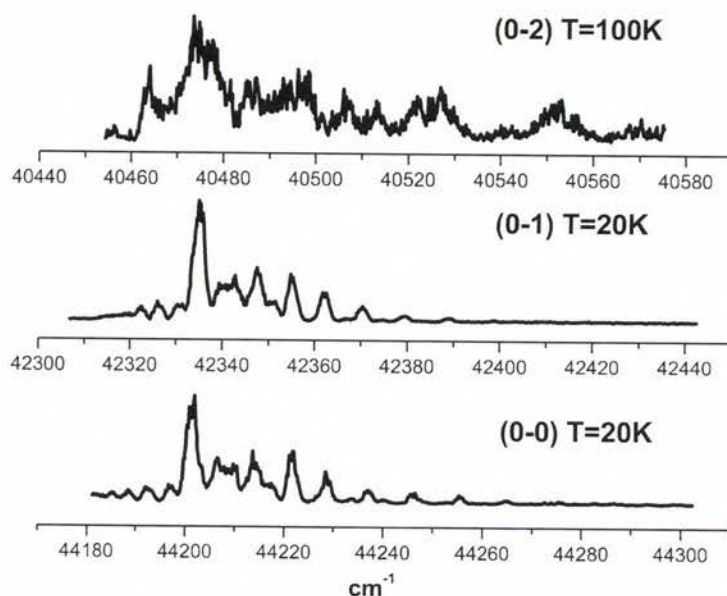


Figure 6.14: One-color (1+1) R2PI spectra of the vibronic transitions [$A^2\Sigma^+ (v'=0) \leftarrow X^2\Pi (v''=0,1,2)$] of the NO product from the excited electronic state decomposition of DAF molecule. Rotational temperature simulations with Boltzmann distribution show that the $v''=0$ and 1 vibrational levels on the ground electronic state have a similar rotational temperature of 20 K, and the $v''=2$ vibrational level has a rotational temperature of 100 K.

Excited electronic state decomposition of the furazan molecule generates NO products with only $v''=0$ and 1 populations, and the spectra of the two observed vibronic bands, (0-0) and (0-1), of the NO product are illustrated in Figure 6.15. The spectral structure of the (0-0) band of the NO product from furazan is similar to that of the NO product from both DAAF and DAF; however, the (0-1) vibronic band shows a hot rotational pattern with a temperature of about 130 K. No (0-3) spectrum of NO from DAF and (0-2) spectrum of NO from furazan are obtained.

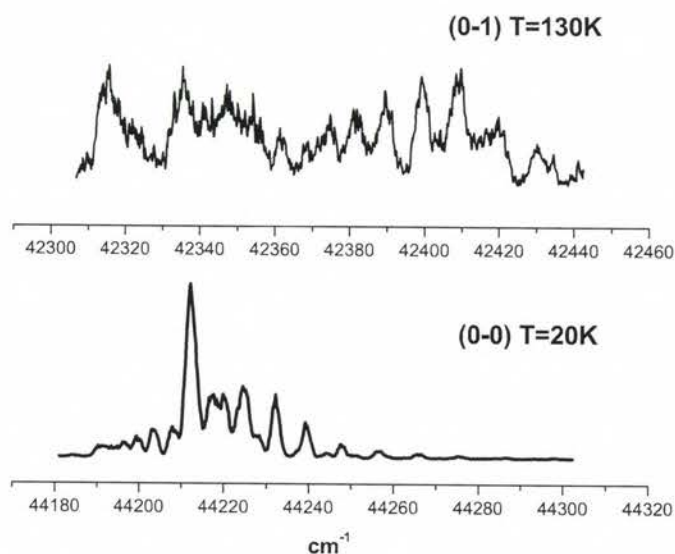


Figure 6.15: One-color (1+1) R2PI spectra of the vibronic transitions [$A^2\Sigma^+ (v'=0) \leftarrow X^2\Pi (v''=0,1)$] of the NO product from the excited electronic state decomposition of furazan molecule. Rotational temperature simulations with Boltzmann distribution show that the $v''=0$ vibrational level on the ground electronic states have a rotational temperature of 20 K, and the $v''=1$ vibrational level has a rotational temperature of 130 K.

Thus, experimental results show that the furazan based model systems show excitation wavelength dependent dissociation channels. For example, dissociation of furazan at 236 nm and DAF at 248 nm renders hot rotational distributions for the NO product, whereas excitation of furazan at 226 nm and DAF at 226 and 236 nm yields cold rotational distributions for the NO fragmentation product.

Theoretical calculations using CASMP2//CASSCF/6-31G(d) level of theory predict two different possible nonadiabatic pathways for excited electronic state decomposition of DAF and furazan: (a) ring contraction through the $(S_1/S_0)_{Cl,a}$ and (b) ring opening through the $(S_1/S_0)_{Cl,b}$. A schematic one dimensional projection of multidimensional potential energy surfaces of furazan and DAF are plotted in Figures 6.16 A and B, respectively. Dotted arrows in the figures indicate possible different

pathways for these two molecules. Surfaces are computed at CASSCF/6-31G* level of theory and the critical points on the surfaces are computed at CASMP2//CASSCF/6-31G* level of theory.

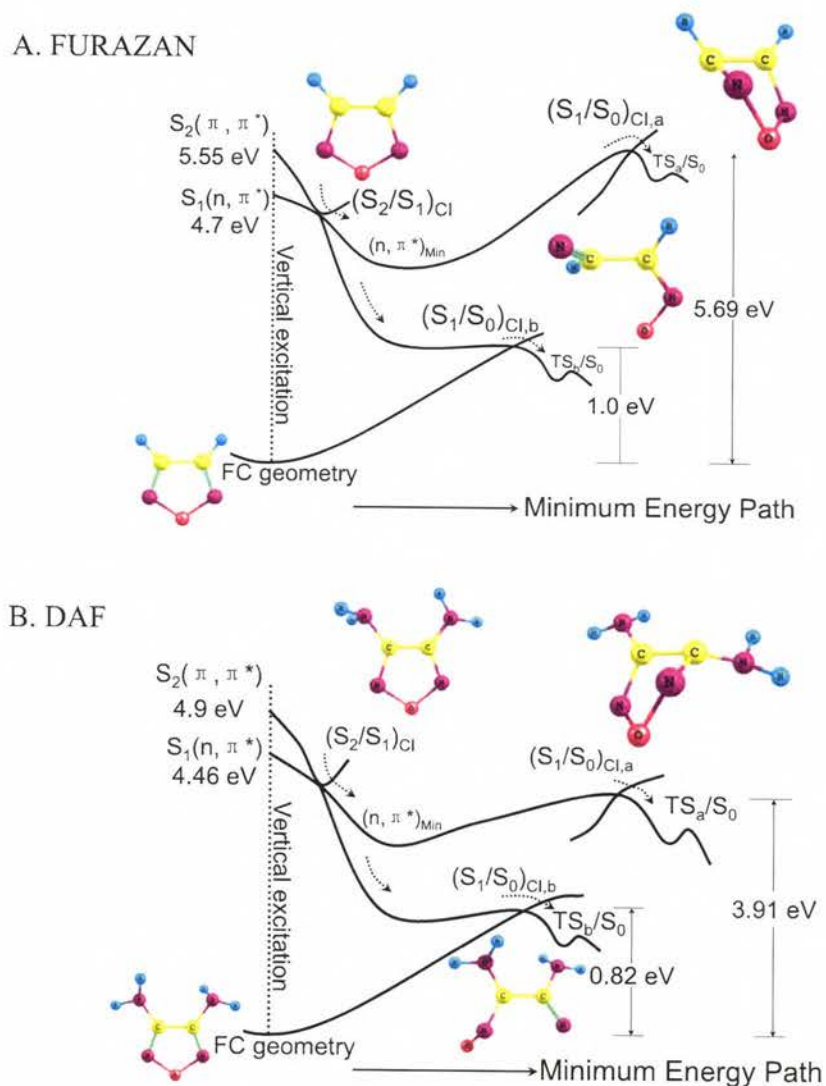


Figure 6.16: One dimensional projection of multidimensional potential energy surfaces of furazan (A) and DAF (B) computed at CASSCF/6-31G* level of theory. Energies of the critical points and conical intersections are computed at CASMP2//CASSCF/6-31G* level of theory. An $(S_1/S_0)_{Cl,a}$ conical intersection is involved in the ring contraction pathway, which can lead the generation of rotationally cold NO initial product. Another $(S_1/S_0)_{Cl,b}$ conical intersection is involved in ring opening pathway, which can finally yield a rotationally hot distribution for the NO product. Note that two nonadiabatic dissociation channels are along two different nuclear co-ordinates.

The furazan molecule is excited to its $S_2(\pi,\pi^*)$ excited state by the excitation energies (5.49 eV, 5.26 eV, and 5.00 eV) used in the experiment. For furazan (see Figure 4.9 A) the $(S_1/S_0)_{CI,a}$ conical intersection is found to have an almost similar (within usual energy uncertainty of $\sim\pm 0.1$ eV in CASMP2//CASSCF computation) energy as that of the absorption maximum energy of the spectroscopically active $S_2(\pi,\pi^*)$ state. Therefore, following electronic excitation to the $S_2(\pi,\pi^*)$ state of furazan at 5.49 eV, the molecule can access a ring contraction nonadiabatic pathway from the FC point of its $S_2(\pi,\pi^*)$ state through $(S_1/S_0)_{CI,a}$ after crossing the $(S_2/S_1)_{CI}$ CI. Following this pathway furazan comes back to the ground state and dissociates through an NO elimination pathway. The transition state (TS) associated with NO elimination on the ground electronic surface of this molecule possesses an unstable vibrational mode which illustrates an NO-azirene(C_2H_2N) symmetric stretch. As no torque acts on the NO moiety at the NO elimination TS, formation rotationally cold NO product from furazan following electronic excitation at 5.49 eV is predicted by the present CASSCF computation.

Furazan cannot surmount the energy barrier for the $(S_1/S_0)_{CI}$ conical intersection while it is excited at 5.26 eV (236 nm) since this excitation energy is about 0.43 eV lower than that of the energy barrier to the $(S_1/S_0)_{CI,a}$ CI. Rather, electronic excitation at 5.26 eV is predicted to lead the molecule to the $(S_1/S_0)_{CI,b}$ after crossing $(S_2/S_1)_{CI}$. This nonadiabatic pathway is associated with a ring opening mechanism and finally brings the molecule to the ground state. On the ground state, furazan subsequently dissociates through NO elimination pathway. This pathway can result in a rotationally hot distribution of the NO, as the NO elimination TS on the ground electronic state surface

following the $(S_1/S_0)_{CI,b}$ conical intersection is associated with an unstable normal mode of vibration which generates a torque on the NO moiety during dissociation. Thus, theoretical calculations suggest that excited electronic state decomposition of furazan at 5.49 eV (226 nm) and 5.26 eV (236 nm) electronic excitations involves two different nonadiabatic dissociation pathways: one yielding rotationally cold NO as initial decomposition product through $(S_1/S_0)_{CI,a}$ and another generating rotationally hot NO as initial decomposition product through $(S_1/S_0)_{CI,b}$.

For DAF, the absorption maximum energy of the spectroscopically active $S_2(\pi,\pi^*)$ state is calculated to be 4.9 eV at the CASMP2//CASSCF/6-31G* level of theory. This level of theory predicts an energy which is ~0.5 eV lower than that of experimental absorption maximum value (obtained in methanol solution) of ~5.4 eV for DAF. Therefore, direct comparison of the computed excitation energies of DAF and experimental excitation energies used in the present experiments is not possible; however, relative energies of the conical intersections with respect to the FC point of the $S_2(\pi,\pi^*)$ state of this molecule depicts the similar decomposition picture for DAF as that is observed in the experiment.

The $(S_1/S_0)_{CI,a}$ conical intersection (in Fig. 6.16 B) is predicted to be lower in energy than the vertical excitation energy of the $S_2(\pi,\pi^*)$ state. The energy difference between FC point of the $S_2(\pi,\pi^*)$ state and the $(S_1/S_0)_{CI,a}$ conical intersection is predicted to be ~1 eV (ca. the energy uncertainty of the computation) at CASMP2//CASSCF/6-31G* level of theory. This makes the $(S_1/S_0)_{CI,a}$ conical intersection energetically accessible from even much below the FC point of the $S_2(\pi,\pi^*)$ state. Thus, electronic excitation of DAF at even below 5.49 eV photoexcitations

is still expected to follow the ring contraction nonadiabatic pathway through $(S_1/S_0)_{Cl,a}$. This theoretical prediction is consistent with the experimental observation. Experimental results infer that dissociation DAF at 5.49 and 5.24 eV occurs through the same decomposition pathway which yields cold rotational distributions of the NO product. Decomposition of DAF at 5.00 eV, however, follows different pathway generating rotationally hot distributions of the NO product. This pathway undoubtedly involves ring opening mechanism through $(S_1/S_0)_{Cl,b}$.

Conclusions. Excited electronic state decomposition of DAAF generates only rotationally cold (20 K) distributions of the NO product at different excitation energies (5.49 eV, 5.26 eV, and 5.00 eV). This implies that excited electronic state decomposition of DAAF follows a single, excitation wavelength independent, dissociation channel. A similar single, excitation wavelength independent dissociation channel is also observed from RDX, HMX, and CL-20. This behavior of energetic materials can be rationalized by the fact that DAAF must have dissociative excited states which can provide a barrierless single decay channel for excited state decomposition. The model systems (furazan and DAF), on the other hand, show excitation wavelength dependent dissociation channels. Electronic excitation of furazan at 226 nm and DAF at 226 and 236 nm yields cold rotational distributions for the NO fragmentation product and dissociation of furazan at 236 nm and DAF at 248 nm renders hot rotational distributions for the NO product. Theoretical calculations show that a ring contraction mechanism is involved through $(S_1/S_0)_{Cl,a}$ to generate rotationally cold NO product and that a ring opening mechanism is involved through $(S_1/S_0)_{Cl,b}$ to generate rotationally hot distributions of the NO product. Thus, excitation

wavelength dependent decomposition channels of the model systems are the result of their specific nonadiabatic chemistry through different conical intersections.

Detailed theoretical exploration of nonadiabatic chemistry of DAAF is not possible using present computational capabilities because a large active space is required for CASSCF calculations for DAAF. Nonetheless, experimental observations provide a number of important insights about the nonadiabatic chemistry of DAAF. DAAF has generated only rotationally cold (20 K) distributions of NO product following electronic excitation at three different excitation energies. In comparison with the model system behavior, a rotationally cold distribution of the NO product is generated through the ring contraction mechanism and an $(S_1/S_0)_{CI,a}$ (similar to the $(S_1/S_0)_{CI,a}$ for DAF and furazan) are involved in this decomposition pathway. Similar rotational distributions of the NO product obtained at different excitation energies indicate that excited electronic states of DAAF are dissociative in nature. Furthermore, the $(S_1/S_0)_{CI,a}$ conical intersection of DAAF is even much lower in energy than that of FC point energy so that the suggested $(S_1/S_0)_{CI,a}$ conical intersection in the ring contraction reaction coordinate can be readily accessible by electronic excitations at all of the three excitation wavelengths used in our experiment. This energetically accessible conical intersection can provide DAAF a very efficient, unique, and single pathway to release its entire chemical energy from random electronic excitations to its (π,π^*) excited electronic state during the detonation of this energetic material. The model systems, on the other hand, suffer from not having an efficient single pathway to release their entire chemical energy during excited electronic state decompositions of these species. One pathway for the model systems provides rotationally cold NO

product; another provides rotationally hot NO product. Thereby, the energy barrier for the $(S_1/S_0)_{CI,a}$ conical intersection in the ring contraction reaction coordinate with respect to the excitation wavelengths plays a crucial role in the decomposition mechanism of these molecules.

6.6 Nonadiabatic Chemistry of Tetrazine-N-Oxides

Recently, high nitrogen content energetic materials have received increased attention due to their novel energetic and explosive properties. Tetrazine-N-oxide, a high nitrogen content molecule, is one of the many nitrogen rich heterocyclic frameworks on which a number of high nitrogen content energetic materials are based. For instance, 3,3'-azobis(6-amino-1,2,4,5-tetrazine)-mixed N-oxides (DAATO_{3,5}, structure illustrated in Figure 6.17) is a tetrazine-N-oxide based nitrogen rich energetic material, which has recently received increased attention due in large part to its extremely high burn rate and low dependency on pressure. This molecule has an average oxygen content of about 3.5. Another two important tetrazine-N-oxide based energetic molecules are 3-amino-6-chloro-1,2,4,5-tetrazine-2,4-dioxide (ACTO, structure in Figure 6.17) and 3,6-diamino-1,2,4,5-tetrazine-1,4-dioxide (DATO, structure in Figure 6.17), which have been relatively unexploited for use as energetic materials.

DAATO_{3,5} and ACTO differ from DATO mainly by the relative position of the oxygen atom attached to the tetrazine ring. DAATO_{3,5} and ACTO possess a tetrazine-2,4-dioxide moiety, whereas DATO has a tetrazine-1,4-dioxide moiety. In the following discussion, we shall see that for these tetrazine-N-oxide based energetic materials the relative position of the oxygen atom attached to the tetrazine ring is

important parameter along with their nonadiabatic chemistry which controls their energetic behavior.

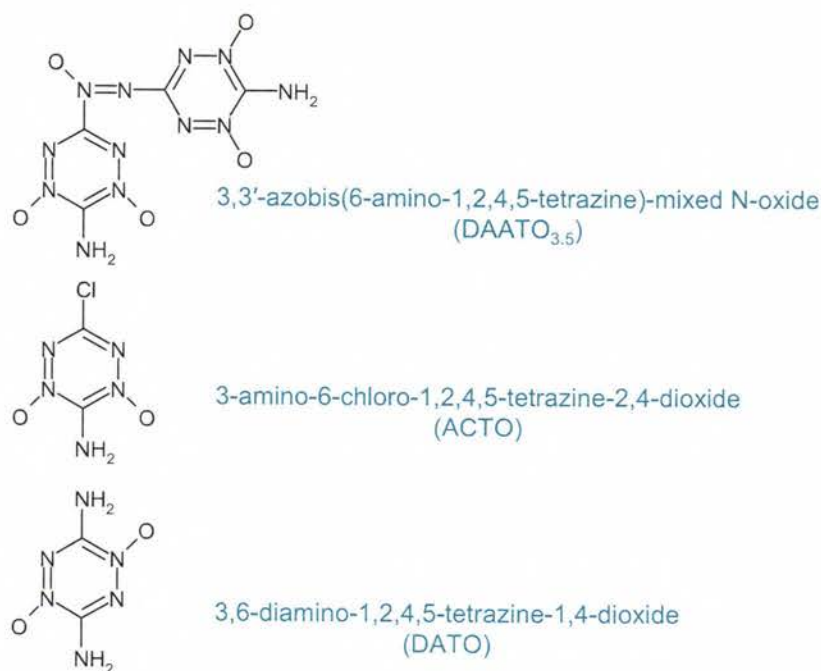


Figure 6.17: Chemical structures of tetrazine-N-oxide based energetic molecules: DAATO_{3.5}, ACTO, and DATO.

DAATO_{3.5}, ACTO, and DATO – Results and Discussions. NO product is observed following excited electronic state decomposition of all the tetrazine-N-oxide based molecules. (1+1) R2PI spectra of the three vibronic transitions, $A^2\Sigma^+(v'=0) \leftarrow X^2\Pi(v''=0,1,2)$ of the NO product observed from excited electronic state decomposition of DAATO_{3.5} are shown in Figure 6.18. Spectral simulations based on Boltzmann population distributions for the three vibronic transitions produce similar cold rotational temperatures of 20 K and a vibrational temperature of 1200 K. Similar (1+1) R2PI spectra of three vibronic transitions, $A^2\Sigma^+(v'=0) \leftarrow X^2\Pi(v''=0,1,2)$ of the NO molecule are obtained from excited electronic state decomposition of ACTO. The (0-0),

(0-1), and (0-2) vibronic bands of the NO product from ACTO show similar rotational patterns to those of the NO product from DAATO_{3.5}, and the rotational temperature of these bands is also about 20 K. The excited electronic state decomposition of the DATO also generates an NO product, however, with only a $v''=0$ population. The (1+1) R2PI spectrum of the (0-0) vibronic band of the NO product from DATO is illustrated in Figure 6.19 which shows a hotter rotational pattern with a temperature of about 50 K.

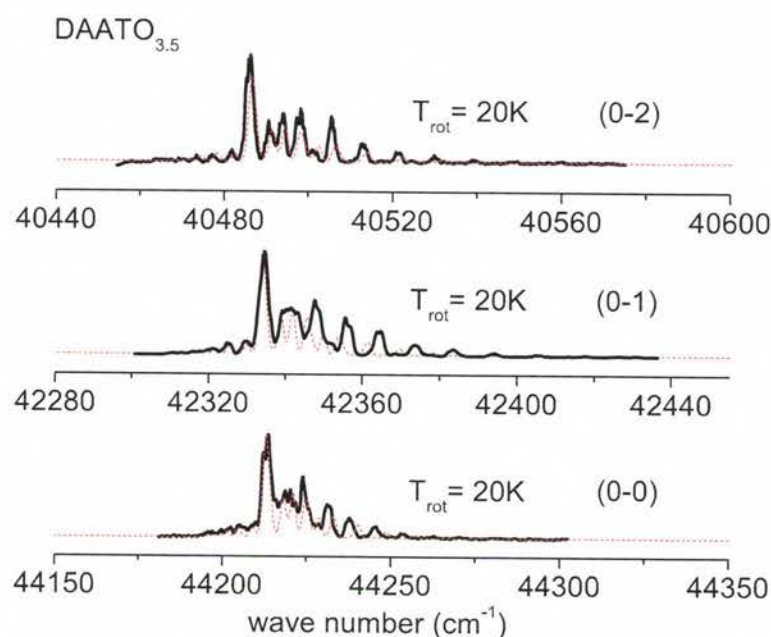


Figure 6.18: One color (1+1) R2PI spectra of the vibronic transitions $A^2\Sigma^+(v'=0) \leftarrow X^2\Pi(v''=0,1,2)$ of the NO product from the excited electronic state decomposition of DAATO_{3.5}. Rotational temperature simulations with a Boltzmann population distributions show that the three observed vibrational levels on the ground electronic states have a similar rotational temperature of ca. 20 K.

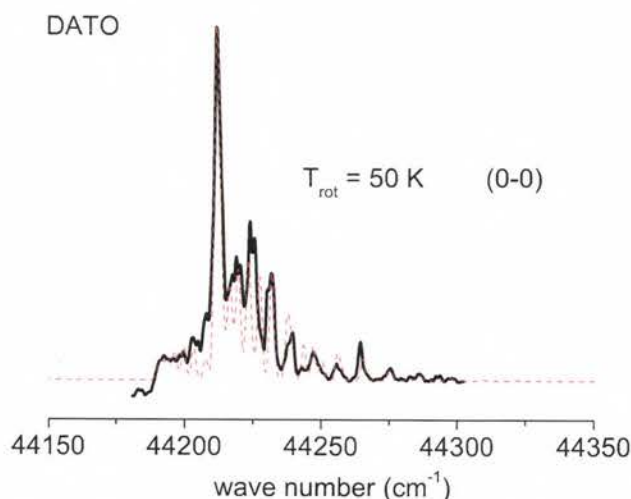


Figure 6.19: One color (1+1) R2PI spectra of the vibronic transitions $A^2\Sigma^+(v'=0) \leftarrow X^2\Pi(v''=0)$ of the NO product from the excited electronic state decomposition of DATO. Rotational temperature simulation with Boltzmann population distributions estimates a rotational temperature of ca. 50 K

The theoretical results at the CASSCF level of theory show that a nonadiabatic pathway through a ring contraction mechanism is involved in generation of an NO product from excited electronic state decomposition of ACTO and DATO. Ring contraction takes place near the $(S_1/S_0)_{CI}$ conical intersection as these molecules evolve from low lying excited electronic states to the ground state. A schematic one-dimensional projection of the multidimensional singlet potential energy surfaces (S_0 , S_1 , S_2 , and S_3) of ACTO with locations and structures of different critical points and conical intersections following the ring contraction pathway, computed at CASSCF/6-31G(d) level of theory is plotted in Figure 6.20. Comparison of computed vertical excitation energies and the experimental excitation energies (5.49 eV, 5.24 eV, and 5.00 eV) infers that electronic excitation of ACTO at 5.49 eV excites the molecule to the S_2 state. Following vertical excitation to the FC point of the S_2 surface, ACTO can

undergo rapid nonadiabatic internal conversion through the $(S_2/S_1)_{Cl}$ conical intersection. These nonadiabatic state changes occur without significant change in nuclear configuration (molecular geometry).

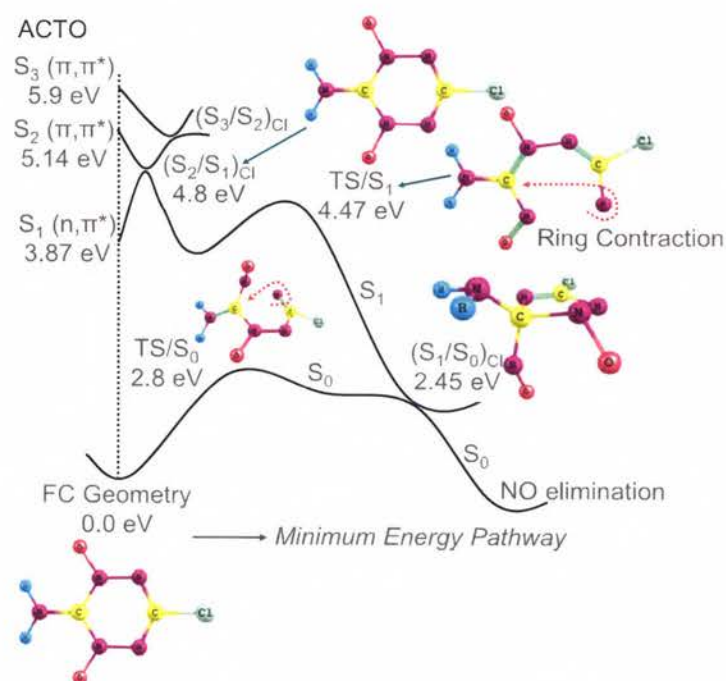


Figure 6.20: One dimensional projection of the multidimensional singlet electronic potential energy surfaces of ACTO computed at CASSCF(10,8)/6-31G(d) level of theory. Geometry near the $(S_1/S_0)_{Cl}$ supports a ring contraction mechanism for excited electronic state decomposition of ACTO, which finally results in NO elimination. Note that ring contracted form of ACTO near the $(S_1/S_0)_{Cl}$ has nearly linear C-NO moiety attached to the triazole ring, which can finally generate a rotationally cold NO product.

Following internal conversion to the S_1 surface of ACTO, under isolated molecular beam conditions, the excitation energy is stored in the vibrational degrees of freedom of the molecule on the S_1 surface. Therefore, a ring contraction excited electronic state process can be initiated on the S_1 surface of ACTO. On the S_1 surface, the activation barrier (at 4.47 eV with respect to the S_0 FC point, (see Figure 6.20) for ring contraction of ACTO can easily be surmounted because the excess energy stored in the vibrational degrees of freedom of the S_1 molecule, following radiationless internal

conversion of the ACTO to the S_1 surface, is sufficient to surmount the barrier. Following this transition state, the molecule is directed to the $(S_1/S_0)_{CI}$ and relaxes back to S_0 surface upon which NO elimination takes place with no activation barrier. Thereby, in brief, the ring contraction of the electronically excited ACTO, which leads to the formation of ground state NO as an initial decomposition product, begins on the S_1 surface and develops through the $(S_1/S_0)_{CI}$. Thus this pathway is electronically nonadiabatic.

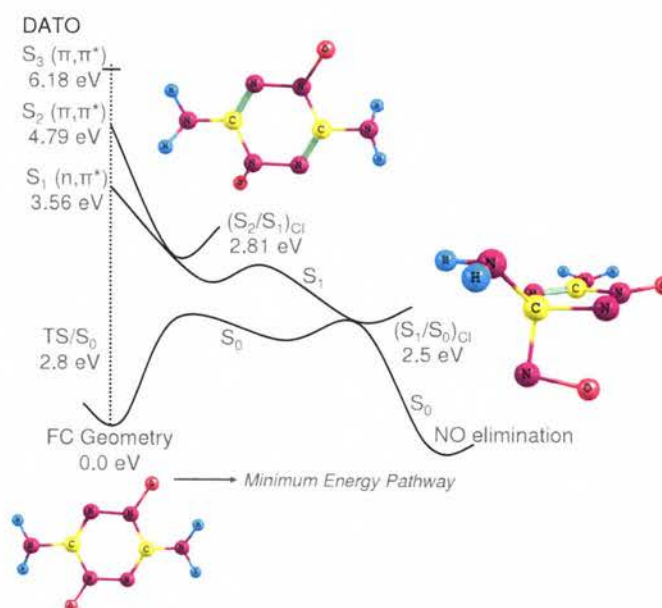


Figure 6.21: One dimensional projection of the multidimensional singlet electronic potential energy surfaces of DATO computed at CASSCF(10,8)/6-31G(d) level of theory. Geometry near the $(S_1/S_0)_{CI}$ supports a ring contraction mechanism for excited electronic state decomposition of DATO, which finally results in NO elimination. Note that ring contracted form of DATO near the $(S_1/S_0)_{CI}$ has a bent C-NO moiety attached to the triazole ring, which can finally generate a rotationally hot NO product.

A similar one-dimensional projection of the multidimensional singlet potential energy surfaces (S_0 , S_1 , and S_2) of DATO with locations and structures of different critical points and conical intersections following the ring contraction pathway,

computed at CASSCF/6-31G(d) level of theory is plotted in Figure 6.21. Comparison of computed vertical excitation energy and the experimental excitation energies indicates that excitation of DATO at 5.49 eV promotes the molecule to the S_2 surface. Following the excitation to the S_2 surface of DATO, the molecule can undergo rapid nonadiabatic internal conversion from S_2 to S_1 through the $(S_2/S_1)_{CI}$ conical intersection. Thereafter, on the S_1 surface, ring contraction pathway is followed and the molecule is further directed to the $(S_1/S_0)_{CI}$. The molecule then relaxes back to the S_0 surface upon which NO elimination takes place with no activation barrier.

Conclusions. Nitric oxide (NO) is observed to be an initial decomposition product from DAATO_{3.5}, ACTO, and DATO. Excited electronic state decomposition of DAATO_{3.5}, and ACTO produces a vibrationally hotter ($T_{vib} \sim 1200$ K), but rotationally colder ($T_{rot} \sim 20$ K) fragment NO product compared to that from DATO, which generates a vibrationally colder (only (0-0) transition of NO is observed), but rotationally hotter ($T_{rot} \sim 50$ K) NO product. The relative positions of the oxygen atoms attached to the ring have significant effect on the final energy distribution among product molecules following decomposition of tetrazine-N-oxide based molecules. Theoretical calculation shows that an $(S_1/S_0)_{CI}$ conical intersection is involved in the excited electronic state decomposition of N-oxide based energetic molecules and that the NO product is generated through a ring contraction mechanism. Furthermore, these high nitrogen content energetic materials decompose from the excited electronic states in a fashion similar to that found for nitramine energetic materials; that is, through series of conical intersections to their ground electronic states. Thus nonadiabatic chemistry controls and

determines the fate of excited electronic state decomposition of high nitrogen content energetic materials.

6.7 General Conclusions

In this chapter the crossing of electronic states, in particular, the ubiquity and role of CIs in decomposition of energetic systems are recognized utilizing the synergism between experiment and theory. Electronically nonadiabatic processes through CIs that span multiple electronic states are ubiquitous and can play a central role in the decomposition chemistry of energetic systems. For example, the presence of CI in the nitro-nitrite isomerization reaction coordinate of nitramines leads to nonadiabatic decomposition of nitramines through this pathway following ($\pi^* \leftarrow n$) electronic excitation. Nitroalkanes, however, do not possess any conical intersections in the nitro-nitrite isomerization reaction coordinate: they dissociate mostly through C-NO₂ bond scission. This pathway, however, is also electronically nonadiabatic. Furthermore, furazan based model molecules dissociate through two different decomposition pathways, both of which are electronically nonadiabatic. Energy barriers to CIs with respect to the excitation energy control the overall excited electronic state decomposition behavior of the model systems. No energy barrier exists for the decomposition of energetic materials.

One of the most important implications of a CI in the chemistry of energetic materials is rapid and efficient internal conversion from upper to lower electronic state surfaces through radiationless transition. This internal conversion facilitates rapid conversion of electronic energy (produced from an initiation pulse), belonging to the upper electronic state, to vibrational energy of the lower electronic state, with a

potential time scale of a few femtoseconds. Therefore, the presence of CIs in the decomposition pathways of energetic materials suggests that the initial step in the excited electronic state decomposition of energetic materials is ultrafast. Dynamics of these decompositions will be controlled by the nonadiabatic coupling between different excited electronic potential energy surfaces.

The results presented in this chapter show that synergism between theory and experiment can lead to an enhanced understanding of the role that nonadiabatic chemistry plays in the initial steps of the decomposition of energetic materials. In a broader context, this work raises a few fundamental questions: can we predict explosive or energetic behavior relying on possible pathways for energetic material decomposition by their nonadiabatic processes; and do conical intersections in the excited state decomposition pathways for energetic materials always determine the outcome of the reaction?

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CHAPTER 7

Unfinished Work and Future Directions: Excited Electronic State

Decomposition of High Nitrogen Content Energetic Materials

Part of the work presented in this chapter is to be submitted for publication in “Guo, Y. Q.; Bhattacharya, A.; Bernstein, E. R. *J. Chem. Phys.* **2010.**” Yuanqing and I worked together on the experiments and I worked independently on the theoretical calculations.

7.1 Introduction

Energetic materials with high nitrogen content have received attention due to their novel energetic and explosive properties,¹⁻⁹ and their high heat of formation. Enthalpy of formation of high nitrogen content energetic materials often exceeds 400 kcal/mol. These materials are less sensitive to destructive stimuli such as shock or impact. Furthermore, colorless, inert, nontoxic, and environmentally friendly molecular nitrogen is expected to be the major decomposition product from these materials. Formation of molecular nitrogen as a major decomposition product facilitates the formation of smoke free, ‘reduced-signature’ propellants which are useful for military applications. Therefore, nitrogen rich energetic materials are promising substitutes for

the more traditional nitramine and nitro containing systems, and would be more acceptable than the traditional energetic materials for both industrial and military use in the near future.¹⁰

A number of high-nitrogen content energetic materials as viable candidates for use in high-performance explosive and propellants are known thus far. They include: (1) BTATz, (2) TAGzT, (3) TAGDNATO, and (4) TAGDNAT. The structure of BTATz is given in Figure 7.1 and the structures of the rest of the compounds are illustrated in Figure 7.2. BTATz is a tetrazine/tetrazole based energetic molecule; TAGDNATO, TAGDNAT, and TAGzT are nitrogen rich, guanidinium cation based energetic salts.¹¹

The basic sensitivity and performance of high nitrogen content energetic materials have been evaluated;^{6,8} however, the unimolecular decomposition of these molecules has not been studied thus far. Excited electronic states are proposed to play an important role in the shock wave decomposition of energetic materials:¹² excited electronic states can be created by decreasing the HOMO-LUMO energy gap via compression from the wave front of a shock wave, and by the shearing of crystal planes.¹³ Extensive work on decomposition of energetic materials in our lab has firmly established that conical intersections which arise due to the crossing of multidimensional electronic PESs play an important role in excited electronic state decomposition of these materials.¹⁴⁻¹⁷ This chapter addresses the progress made thus far on theoretical predictions of the excited electronic state decomposition of a nitrogen rich energetic material, BTATz and a nitrogen rich model system, guanidine considering the influence of conical intersections in their decompositions. A future

direction of the experimental work to obtain detailed insight about decomposition of high nitrogen content energetic materials is also discussed here. Theoretical results indicate that N_2 and NH_3 are expected to be major decomposition product of the nitrogen rich energetic systems and guanidine based systems, respectively. Here highly sensitive REMPI detection schemes are presented to probe rovibrational distributions of the products N_2 and NH_3 expected to be generated from these materials. In a nutshell, the future direction of the research presented in this thesis follows exploration of excited electronic state decomposition of nitrogen rich energetic materials through analysis of rovibrational state distributions of the product molecules, and through search for conical intersections in their decomposition pathways.

7.2 Decomposition of BTATz: A Theoretical Prediction

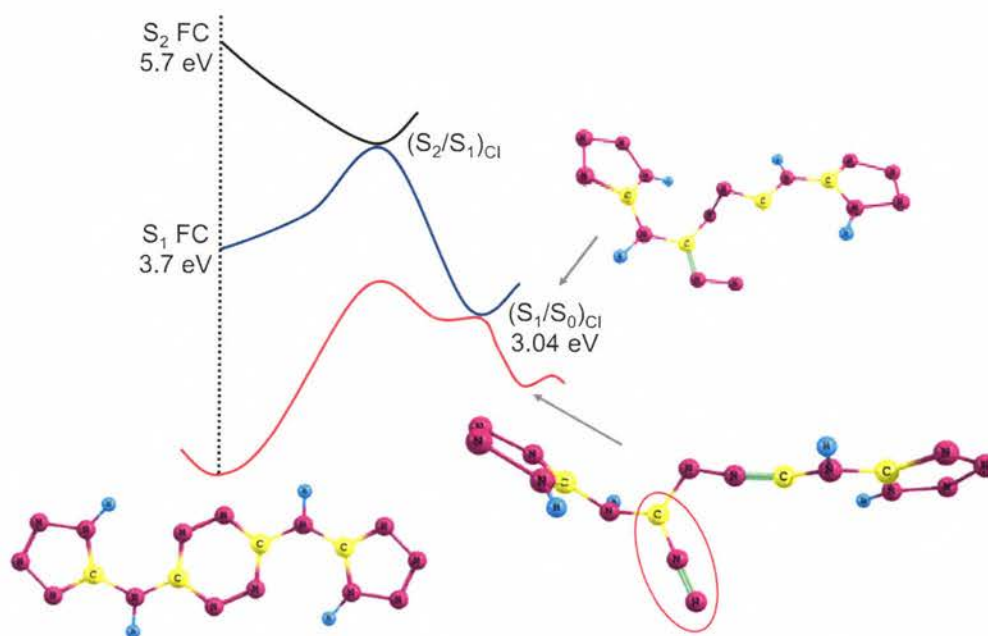
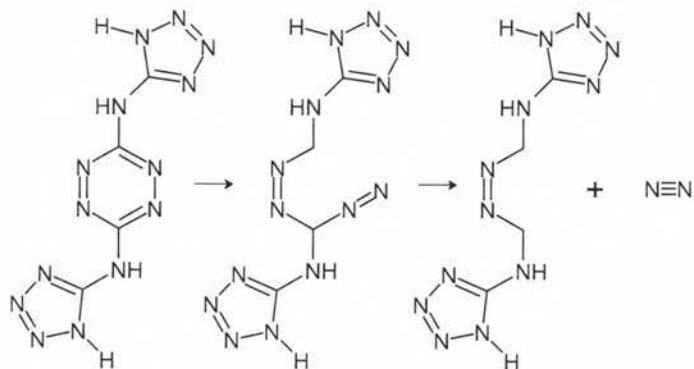


Figure 7.1: One dimensional projection of the multidimensional electronic potential energy surfaces of BTATz, computed at CASSCF(14,11)/STO-3G level of theory. $(S_1/S_0)_{CI}$ predicts a geometry which infers that a tetrazine ring opening mechanism is involved in the initial step of excited electronic state decomposition of this energetic material.

BTATz is a nitrogen rich energetic material with one tetrazine and two tetrazole rings (see Figure 7.1 for structure). The theoretical calculations are performed at the CASSCF(14,11)/STO-3G level of theory, which show that the two lowest lying excited electronic states (S_1 and S_2) for BTATz are of (n,π^*) and (π,π^*) character, respectively. They have vertical excitation energies of 3.7 and 5.7 eV, respectively at this level of theory. The calculated vertical excitation energy of the $S_2(\pi,\pi^*)$ states is not in very good agreement with the experimental absorption maxima of 4.5 eV (see Figure 7.S1 of Supplementary Information for UV-VIS absorption spectrum of BTATz at the end of this chapter). In order to improve the calculation for the vertical excitation energy one can improve the basis set and use a larger active space. In fact, considering only π and nonbonding orbitals, the active space of BTATz should comprise 28 orbitals, but inclusion of such a large active space in the CASSCF computation is beyond the scope of the present capability of quantum mechanical software packages (e.g., Gaussian03 and Molpro). Therefore, although use of (14,11) active space and STO-3G basis set for the computation of BTATz, in principle, is questionable, the present computational effort is the first attempt to explore conical intersections and PESs of a large, truly energetic molecule with the present capability and a compromise between accuracy and cost. Furthermore, often improvement of level of theory improves relative energies between critical points on PESs, but it does not change the geometry drastically.

Potential energy surfaces of BTATz with location of critical points computed at the CASSCF(14,11)/STO-3G level of theory are depicted in Figure 7.1. Based on these calculations, a novel tetrazine ring opening mechanism through an $(S_1/S_0)_{CI}$ conical

intersection is proposed to be involved in the excited electronic state decomposition of BTATz:



This mechanism is finally expected to result in formation of the rotationally cold N_2 product because the molecule possesses a linear C-N=N moiety following opening of the tetrazine ring, and no torque acts on the N_2 during N_2 elimination from the C-N=N moiety on the ground electronic state surface.

7.3 Decomposition of Guanidine: A theoretical Prediction

Guanidine and its derivatives have recently been suggested as possible nitrogen rich building block in novel highly energetic materials.¹¹ In particular, the guanidinium cation based energetic salts have drawn increased attention for the development of high-energy density materials. These salts are intrinsically nonvolatile, and typically thermally stable under normal conditions, and are denser than atomically similar nonionic analogues. Notable guanidinium cation based energetic salts include TAGzT, TAGDNAT, and TAGDNATO. The chemical structures of these energetic salts are illustrated in Figure 7.2. Guanidine is a model system of these energetic salts. Guanidine is also currently being considered as an alternative fuel. The potential advantage for uses of guanidine as fuel is that it is biocompatible and can be supplied very easily because pure guanidine is low melting solid (melting point $\sim 50^\circ\text{C}$).

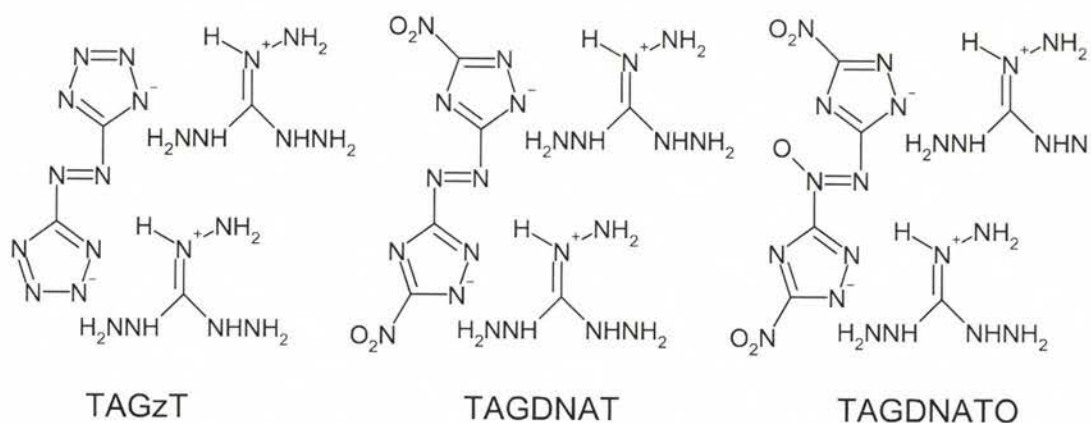
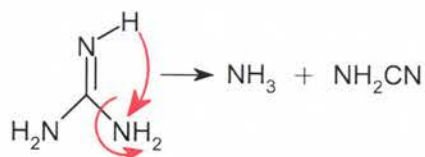


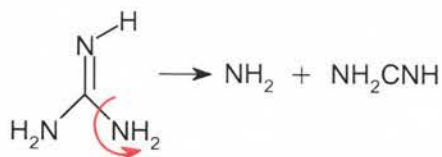
Figure 7.2: Guanidinium cation based energetic salts: Triaminoguanidinium azotetrazolate (TAGzT), Bis-triaminoguanidinium-(3,3'-dinitroazotriazolate) (TAGDNAT), and triaminoguanidinium-(3,3'-dinitroazoxy-1,2,4-triazolate) (TAGDNATO).

Two possible decomposition pathways of guanidine are suggested:

1. NH_3 elimination:



2. NH_2 elimination:



To find which of the above two possible decomposition pathways is involved in the excited electronic state decomposition of isolated guanidine, theoretical computation at the CASSCF level of theory is performed for guanidine. A one dimensional projection of the multidimensional potential energy surfaces of guanidine computed at CASMP2//CASSCF(14,11)/6-31G(d) level of theory is depicted in Figure 7.3.

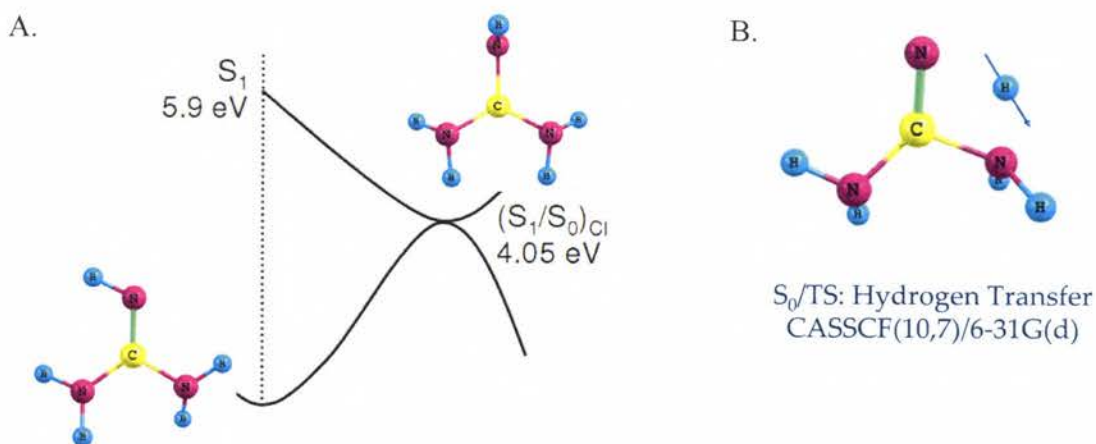


Figure 7.3: A. one dimensional projection of the multidimensional potential energy surfaces with $(S_1/S_0)_{CI}$ of guanidine computed at CASMP2//CASSCF(14,11)/6-31G(d) level of theory. B. Hydrogen transfer TS on the S_0 surface of guanidine computed at CASSCF(10,7)/6-31G(d) level of theory.

Theoretical results predict that NH_3 elimination is expected to be involved in the excited electronic state decomposition of guanidine. An $(S_1/S_0)_{CI}$ is responsible for the initial internal conversion of the molecule from the S_1 state to the ground state S_0 , and subsequently for an intramolecular hydrogen transfer on the ground state surface. This pathway finally yields an NH_3 product molecule.

7.4 Detection of N_2 through REMPI:

Nitrogen molecules are expected to be a major product from decomposition of high nitrogen content energetic materials. Therefore, to study excited electronic state decomposition of nitrogen rich energetic materials, rovibrational-state resolved detection of N_2 is absolutely necessary. Two REMPI schemes are utilized employing two different electronic transitions of N_2 for rovibrational-state resolved detection of N_2 in TOFMS: (1) (2+2) REMPI employing the $N_2^+ \leftarrow \tilde{a}^1\Pi_g \leftarrow \tilde{X}^1\Sigma_g^+$ electronic transition; and (2) (2+1) REMPI employing the $N_2^+ \leftarrow a''^1\Sigma_g^+ \leftarrow \tilde{X}^1\Sigma_g^+$ electronic

transition. Details of the detection scheme of N_2 and rotational temperature determination can be found in Appendix II.

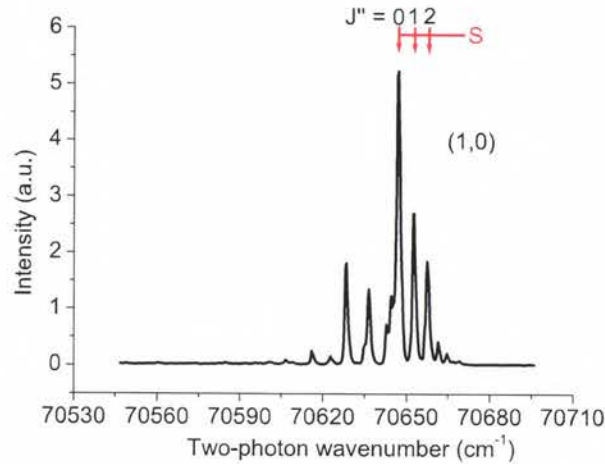


Figure 7.4: (2+2) REMPI spectrum of N_2 from 1% N_2 in He gas mixture, observed around the (1,0) band head of the $\tilde{a}^1\Pi_g(v'=1) \leftarrow \tilde{X}^1\Sigma_g^+(v''=0)$ electronic transition near 283 nm. Rotational temperature is estimated to be 10 K.

The (2+2) REMPI spectrum of N_2 obtained from a $\sim 1\%$ N_2 in He gas mixture, observed around the (1,0) band head of the two photon $\tilde{a}^1\Pi_g(v'=1) \leftarrow \tilde{X}^1\Sigma_g^+(v''=0)$ electronic transition near 283 nm, is shown in Figure 7.4. The most intense feature in the spectrum belongs to S-branch ($\Delta J = +2$) of the (1,0) band. The (2+1) REMPI spectrum of N_2 observed around the (0,0) band head of the $a''^1\Sigma_g^+(v'=0) \leftarrow \tilde{X}^1\Sigma_g^+(v''=0)$ electronic transition near 203 nm is shown in Figure 7.5. All of the spectral features in the spectrum belong to the Q-branch of the (0,0) band of the two-photon $a''^1\Sigma_g^+ \leftarrow \tilde{X}^1\Sigma_g^+$ electronic transition of N_2 .

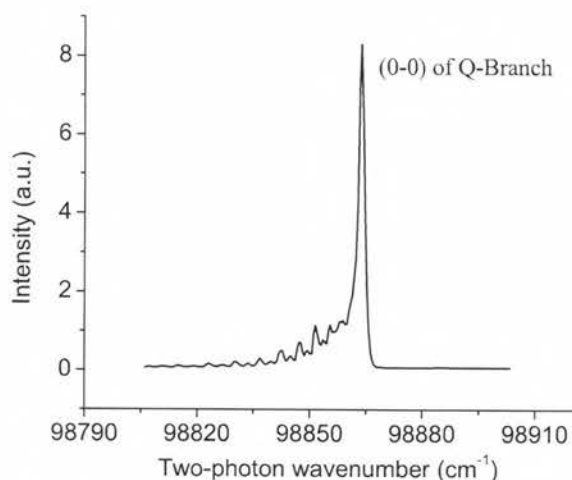


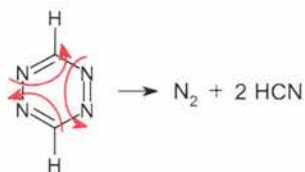
Figure 7.5: (2+1) REMPI spectrum of N_2 from 1% N_2 in He gas mixture, observed around (0,0) band head of $a''^1\Sigma_g^+(v'=0) \leftarrow \tilde{X}^1\Sigma_g^+(v''=0)$ electronic transition near 203 nm.

Therefore, the above results indicate that both (2+2) and (2+1) REMPI techniques can be potentially applied to study excited electronic state decomposition of high nitrogen content energetic materials in future. The (2+1) REMPI scheme has additional advantage over (2+2) REMPI scheme. The (2+1) REMPI scheme is found to have about three orders of magnitude higher N_2 detection sensitivity over that of (2+2) REMPI scheme. Furthermore, most of the high nitrogen content energetic materials have strong UV absorption near 203 nm, which is used for (2+1) REMPI detection scheme. Thus, if 203 nm light is used, only a single laser beam can be used to dissociate the parent molecule and detect the N_2 product. Future direction of the reach presented in the part 1 of this thesis is to probe rovibrational state distribution of the N_2 product from decomposition of high nitrogen content energetic materials.

7.5 Decomposition of Tetrazine Based Molecules at 203 nm:

Excited electronic state decomposition of the tetrazine has been intensively investigated both experimentally and theoretically.¹⁸ To date, N_2 is undoubtedly

corroborated to be the initial photodecomposition product; however, different experiments support different mechanisms (either concerted or step-wise) for this photodissociation reaction:



No experiment thus far has measured rovibrational distributions of the N_2 product generated from excited electronic state decomposition of tetrazine. In the present effort, N_2 product from photodecomposition of tetrazine at 203 nm is detected and its rotational state distribution is analyzed utilizing the (2+1) REMPI scheme mentioned above.

Nitrogen is an abundant molecule in air and even at 2×10^{-7} Torr background pressure in the TOFMS chamber, 500 mV of N_2 signal is observed when 2700 V is used for MCP detector. When tetrazine is dissociated at 203 nm, the TOFM signal of N_2 is enhanced from 500 mV to 700 mV. Thus experimentally obtained (2+1) REMPI spectrum of N_2 from photodissociation of tetrazine should contain contribution from the background N_2 . To obtain the N_2 spectrum from only photodecomposition of tetrazine, the background spectrum needs to be subtracted from that (2+1) REMPI spectrum of N_2 . Figure 7.6 illustrates the (2+1) spectra obtained for background N_2 and N_2 from photodissociation of tetrazine, and their subtracted spectrum. All the transitions shown in this figure are Q-branch lines ($\Delta J = 0$) for the two-photon electronic transition $a''^1\Sigma_g^+(v' = 0) \leftarrow \tilde{X}^1\Sigma_g^+(v'' = 0)$.

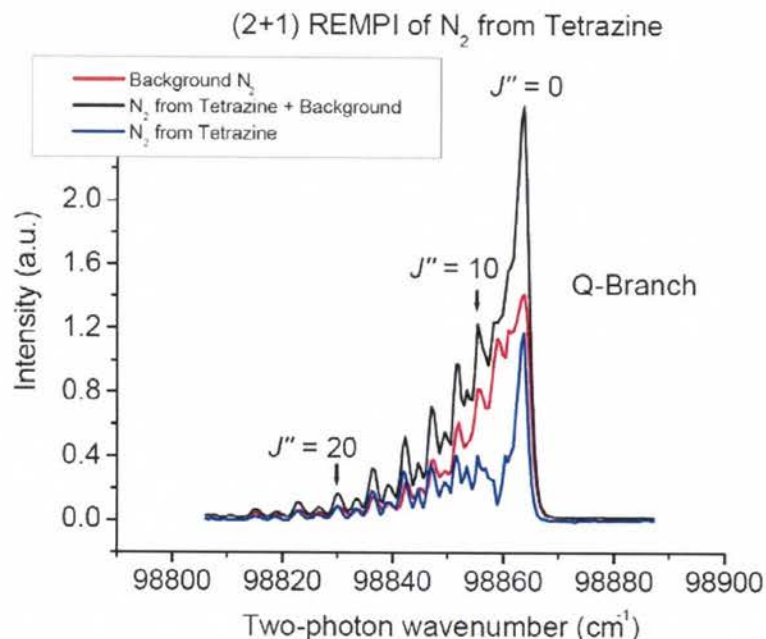
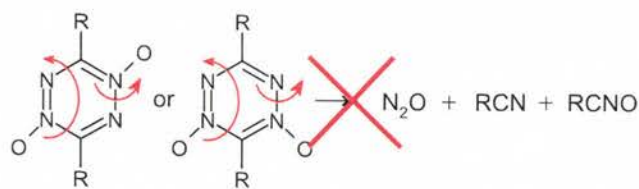


Figure 7.6: (2+1) REMPI spectrum of N_2 from photolysis of tetrazine at 203 nm.

The background spectrum exhibits well-resolved rotational structures up to $J'' > 20$, which provides ~ 300 K rotational temperature based on two-photon transition line strengths and Boltzmann population distributions of the rotational states. The subtracted spectrum arises mostly transition from $J'' = 0$, which provides a rotational temperature of ~ 10 -15 K. Accurate measurement of the rotational temperature of the subtracted spectrum is difficult since the lines for $J'' > 0$ are perturbed in intensity because of the subtraction; however, the subtracted spectrum clearly indicates that N_2 from the photodissociation of tetrazine at 203 nm is rotationally cold (10-15 K).

Observation of rotationally cold N_2 products from decomposition of tetrazine at 203 nm supports triple concerted dissociation pathway because this pathway does not exert any torque on the N_2 moiety. Considering a similar decomposition mechanism, the immediate discernible photodissociation product for tetrazine-N-oxides is predicted to be N_2O .



N_2O can further dissociate and can generate N_2 product. N_2 product from decomposition of N_2O at 203 nm is observed to be rotationally hot (~ 2000 K, see Appendix II). However, no N_2 product is observed from decomposition of tetrazine-N-oxides (such as DAATO_{3.5}, ACTO, and DATO), which essentially infers that decomposition mechanism of tetrazine-N-oxides is different from that of bare tetrazine molecule. In fact, tetrazine-N-oxides dissociate through a ring contraction mechanism, leading to NO elimination in the initial step of their decomposition. Furthermore, no N_2 product is observed from decomposition of other tetrazine based energetic molecules such as BTATz, diaminotetrazine. Understanding the decomposition behavior of these substituted tetrazines requires further study and detection of different species such as NH_2 , CN, etc.

7.6 Detection of NH_3 through REMPI:

NH_3 is expected to be a decomposition product from guanidine and guanidinium cation based energetic systems. Therefore, rovibrational-state resolved detection of NH_3 is of paramount importance to study excited electronic state decomposition of guanidine and guanidinium cation based energetic materials. Here (2+1) REMPI detection scheme can be utilized to detect NH_3 via the $\tilde{\text{C}}'$ Rydberg state of NH_3 at 313 nm. Figure 7.6 displays rotationally resolved spectrum of the $\tilde{\text{C}}' \leftarrow \tilde{\text{X}}^0_{0+}$ band of NH_3 .¹⁹ The Q-branch transitions with $J'' = K''$ are assigned in the figure. The $Q_0(0)$ transition is forbidden and can not be observed due to spin statistical reasons.

Employing this transition an NH_3 product from decomposition of guanidine and gunidinium cation based energetic salts can be detected.

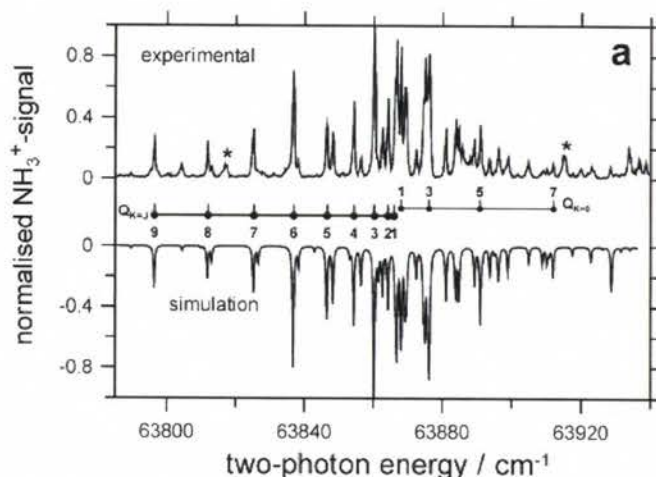


Figure 7.7: $\tilde{C}' \leftarrow \tilde{X} \ 2_{0+}^0$ band of NH_3 . Selected transitions of Q -branch are assigned.¹⁹

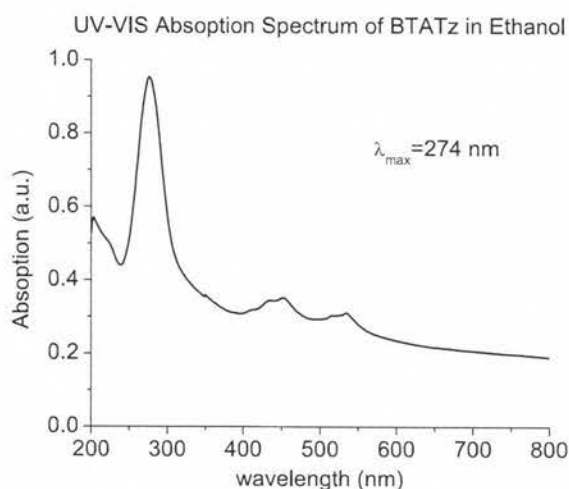
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Supplementary Information

Figure 7.S1: UV-VIS absorption spectrum of BTATz in ethanol



CHAPTER 8

General Conclusions

Excited Electronic State Decomposition of Energetic Molecules

The field of energetic materials has long been considered primarily for its practical aspects in a wide variety of industrial, civil and military applications. It is only recently that the fundamental chemistry and physics of energetic materials at a molecular level, which control the conversion of the energetic molecule to its final products, has begun to emerge. The ultrafast unimolecular decomposition reactions of energetic materials, which are the subject of this thesis, are complex and difficult to study; nonetheless, the work discussed here provides substantial understanding of the behavior of different classes of energetic systems now in use, and provides predictive capabilities for development of new materials.

1. Nitro-Containing Energetic Molecules

Historically, nitro (NO_2) derivatives played a special role as the most commonly used energetic compounds. In spite of having the same NO_2 functional group in the nitro-containing energetic molecules, different X-NO_2 ($\text{X}=\text{C},\text{N}$) bond connectivities in the C-NO_2 (nitroalkane) and N-NO_2 (nitramine) energetic moieties makes them unique and different from each other. In this context, excited electronic state decomposition of dimethylnitramine ($(\text{CH}_3)_2\text{NNO}_2$) and nitromethane (CH_3NO_2) are compared.¹

Decomposition of dimethylnitramine from excited electronic states follows a nitro-nitrite isomerization pathway,² while nitromethane decomposition from excited electronic states follows a C-NO₂ bond dissociation pathway;³ both reactions, however, generate NO as a primary decomposition product. The NO product from the decomposition of dimethylnitramine (N-NO₂) is rotationally and vibrationally colder than that from nitromethane (C-NO₂).¹ This difference raises the intriguing possibility that the N-NO₂ moiety can be better energetic candidate than the C-NO₂ moiety because the N-NO₂ moiety generates internally cold product molecules. In fact, with regard to the sensitivity, in general, nitramines are more sensitive to the shock or impact than are nitroalkanes.⁴

Dimethylnitramine is a simple analogue molecule (model system) of nitramine energetic materials such as RDX, HMX, and CL-20. Nitro-nitrite isomerization is involved in the excited electronic state decomposition of all nitramine species; however, a number of intrinsic differences are found in behavior between nitramine model system and energetic materials.^{5,1} Nitramine model systems dissociate on the excited electronic state and nitramine energetic materials dissociate on the ground state following initial electronic excitation to the low lying excited electronic states. The HONO elimination channel shows a minor contribution to the overall decomposition of the model system dimethylnitramine;² the HONO elimination channel, however, is not involved in the overall decomposition of RDX, HMX or CL-20.⁵ Energetic materials generate rotationally cold (20 K) NO product,⁵ whereas dimethylnitramine produces a rotationally hot (120 K) NO product.²

The NO product generated from decomposition of RDX shows cold rotational (20 K) and hot vibrational (1800 K) distributions. Similar distributions for the product NO are also observed from excited electronic state decomposition of HMX and CL-20.⁵ Therefore, no difference is observed in product internal energy distributions of the different nitramine energetic materials. The ratio of TOFM signal intensity of NO generated from RDX, HMX, and CL-20, however, is estimated to be 3:4:6, which corresponds to the number of nitramine moieties in each molecule, respectively. This result indicates that energetic materials decompose via the same mechanism through which each nitramine energetic group yields a NO molecule. Unimolecular decomposition dynamics of RDX, HMX, and CL-20 from their excited electronic states is faster than 180 fs.

2. Furazan Based Energetic Molecules⁶

Recently, furazan based energetic materials have received great attention due to their favorable properties over traditional energetic systems such as RDX and HMX. Most favorable properties of furazan based energetic species include good heat resistivity, high heat of formation, low sensitivity, and good detonation performance for applications as high explosives, fuels, and propellants. One excellent candidate of this class is DAAF which consists of two amino furazan rings connected by an azoxy group. In accord with nitramine energetic materials, furazan based energetic materials generate NO, as an initial decomposition product, with cold (20 K) rotational distributions. The NO product from furazan based energetic materials, however, shows colder vibrational (1260 K) distributions than that (1800 K) from nitramine energetic materials. Furazan based energetic materials possess excitation wavelength independent single

decomposition channels through a ring contraction mechanism which produces only rotationally cold (20 K) NO product. The furazan based model systems, furazan and DAF, however, show two excitation wavelength dependent decomposition channels. One involves a ring contraction mechanism, which generates rotationally cold (20 K) distribution of the NO product and the other involves a ring opening mechanism, which produces rotationally hot (~100 K) distributions of the NO product. Furthermore, decomposition occurs on the ground state for all furazan based molecules following initial electronic excitation to the low laying electronic states. NH_2 is not an initial decomposition product from any of the furazan based molecules.

3. Tetrazine-N-oxide Based Energetic Molecules⁷

Tetrazine-N-oxide is one of the many nitrogen rich heterocyclic frameworks upon which a number of high nitrogen content energetic materials are based. For instance, 3,3'-azobis(6-amino-1,2,4,5-tetrazine)-mixed-N-oxides ($\text{DAATO}_{3.5}$) is a tetrazine-N-oxide based nitrogen rich energetic material, which has recently received increased attention due in large part to its extremely high burn rate and low dependency on pressure. NO is observed to be an initial product from decomposition of $\text{DAATO}_{3.5}$ similar to nitramine and furazan based energetic materials. The NO product is observed to be rotationally cold (20 K) and vibrationally colder than that from nitramine energetic materials. Similar rotational and vibrational distributions of the NO product, however, are observed from excited electronic state decomposition of furazan based energetic molecules.

Another two important tetrazine-N-oxide based energetic molecules are 3-amino-6-chloro-1,2,4,5-tetrazine-2,4-dioxide (ACTO) and 3,6-diamino-1,2,4,5-

tetrazine-1,4-dioxide (DATO). DAATO_{3,5} and ACTO differ from DATO mainly by the relative position of the oxygen atom attached to the tetrazine ring. DAATO_{3,5} and ACTO possess a tetrazine-2,4-dioxide moiety, whereas DATO has a tetrazine-1,4-dioxide moiety. The rotational and vibrational distributions of the NO product from ACTO are similar to those from DAATO_{3,5}; however, DATO shows hotter rotational (50 K) and much colder vibrational distributions than that of ACTO and DAATO_{3,5}. Thus relative position of the oxygen atoms attached to the tetrazine ring can be a controlling factor determining energetic properties of tetrazine-N-oxide based energetic molecules. A ring contraction mechanism is involved in the excited electronic state decomposition of all tetrazine-N-oxide based energetic materials.

4. High Nitrogen Content Energetic Molecules

High nitrogen content energetic materials have promising energetic and explosive properties due to their high heat of formation, less sensitivity to destructive stimuli such as shock or impact, and their expected environmentally friendly molecular nitrogen products. A number of high-nitrogen content energetic materials are known thus far. They include BTATz, TAGzT, TAGDNATO, and TAGDNAT. For predicting influence of conical intersection in the decomposition of high nitrogen content energetic materials, excited electronic potential energy surfaces of BTATz are explored at the CASSCF(14,11)/STO-3G level of theory. BTATz is a tetrazine/tetrazole based energetic species. Theoretical calculation predicts a novel tetrazine ring opening mechanism to be the major decomposition pathway of BTATz. This decomposition occurs through an (S_1/S_0)_{CI}, and rotationally cold N₂ product is predicted to be a major decomposition product. Experimental justification of this decomposition model of

BTATz, however, requires rovibrational state resolved detection of N_2 through (2+2) REMPI employing the $N_2^+ \leftarrow \tilde{a}^1\Pi_g \leftarrow \tilde{X}^1\Sigma_g^+$ electronic transition or (2+1) REMPI employing the $N_2^+ \leftarrow a''^1\Sigma_g^+ \leftarrow \tilde{X}^1\Sigma_g^+$ electronic transition. Both REMPI schemes are successfully applied to detect N_2 with 1-10 ppb detection sensitivity; however, no N_2 is detected from decomposition of high nitrogen content energetic materials thus far. The discrepancy between experiment and theory may arise due to two possible reasons: (1) decomposition of high nitrogen content energetic materials does not produce substantial amount of N_2 product; (2) a low level of theory has been applied to explore the PESs of BTATz. Corroboration of one of these reasons requires further experimental and theoretical study of decomposition of high nitrogen content energetic materials.

5. Role of Conical Intersections in the Decomposition of Energetic Materials¹

To determine role of conical intersections in the decomposition of energetic materials, theoretical exploration of the excited electronic state surfaces for these systems are mandatory. At present, this task is not possible for large and complex energetic materials because multiconfigurational methodologies, which are absolutely essential for exploration of excited electronic state potential energy surfaces, cannot include an active space with up to 30 active orbitals. To circumvent the problem computation using multiconfigurational methodologies are performed for model systems with single energetic moieties of each particular class.

Results gleaned from excited state computation for model systems show that electronically nonadiabatic processes that span multiple electronic states through conical intersections play a central role in the decomposition chemistry of these

systems. For example, a nitro-nitrite isomerization for dimethylnitramine occurs through $(S_2/S_1)_{CI}$ following electronic excitation to its $S_2(n,\pi^*)$ excited state. Pressure, temperature and geometry near $(S_2/S_1)_{CI}$ determines the branching ratio between the two decomposition channels of dimethylnitramine: NO_2 elimination and nitro-nitrite isomerization. An ultrafast (50 fs) internal conversion of this molecule occurs through $(S_1/S_0)_{CI}$ following electronic excitation to its $S_1(n,\pi^*)$ excited state. The dominant decomposition pathway of furazan based model systems, furazan and DAF, is determined by the energy barrier to the $(S_1/S_0)_{CI}$ with respect to the excitation energy. Furthermore, an $(S_1/S_0)_{CI}$ is involved in the excited electronic state decomposition of ACTO and DATO through a ring contraction mechanism.

Thus, the presence of low lying chemically relevant conical intersections provides a direct pathway by which successful excited electronic state chemistry of energetic model systems can occur. Presence of a conical intersection in the decomposition reaction coordinate facilitates rapid and efficient internal conversion from the upper to the lower electronic states through a radiationless transition. This internal conversion leads to rapid conversion of electronic energy belonging to the upper electronic state to the vibrational energy of the lower electronic state, with a potential timescale of a few femtoseconds. In fact, decomposition dynamics of all energetic materials falls below 180 fs. Thus the dynamics of the decomposition of energetic systems are controlled by the nonadiabatic coupling between different electronic potential energy surfaces. The energy barrier to the low lying chemically relevant conical intersection, in principle, would be a determining factor that would make a system more or less “energetic”.

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Part 2: Conformation Specific Reactivity of Radical Cation Intermediates
of Bioactive Molecules

CHAPTER 9

Introduction

Conformation Specific Reactivity of Radical Cation

Intermediates of Bioactive Molecules

Molecular conformers can interconvert via hindered rotations about single bonds, which gives rise to conformational isomerism.¹ Even though the low energy barriers to these processes lead to equilibration at room temperature, the product selectivity seen previously in some reactions has been explained by conformation-specific reaction mechanisms:^{2,3} if reactant molecules differing only in their conformation are located at different positions on potential energy surface (PES), they may undergo different reactions from these distinct regions of the PES. Recently, the conformer-specificity in chemical reactions has been experimentally demonstrated for several molecular systems. These include distinct photodissociation dynamics for *cis* and *gauche* conformers of propanal cations,⁴ photodissociation of *anti*- and *gauche*-1-iodopropane,⁵ and photodissociation of different conformers of alkanethiols.⁶ Conformational selectivity has also been suggested as a means of achieving an alternate tool for reaction control.^{7,8}

The flexibility of three dimensional structures of biomolecules such as amino acids and proteins provides a great conformational diversity. When these conformers

are subjected to biological reactions, the fate of the reactions can also be expected to be dependent upon the detailed molecular structures of the molecules at the beginning of the reactions. Recently single-molecule methods have been used to investigate conformation-specific, distinctly different rates in key steps of enzymatic processes.^{9,10} Therefore, understanding the relationship between conformer, structure and biochemical reactivity of the flexible biomolecules is essential for understanding and control of biological reactions. In particular, a detail characterization of the conformation-specific reactivity of radical cation intermediates of biomolecules is important because these reactive intermediates induced by oxidative stress are directly involved in the development of a wide range of human diseases including Alzheimer's disease, Parkinson disease, and cancer, as well as in the process of aging.¹¹⁻¹⁴ Understanding conformer specificity in the reactivity of isolated amino acids, hydroxy acids, amides, peptides, and proteins would be an invaluable aid in understanding conformer selective oxidative stress in more complex biological systems at a molecular level. Only a few limited instances of possible conformer-selective dynamics of isolated radical cation intermediates of biomolecules have appeared in the literature.¹⁵⁻¹⁷

Recently, Kim and coworkers have found isolated α -alanine and β -alanine, which are biological building blocks, to be quite conformer-specific in their decarboxylation reactions after formation of radical cations.¹⁶ A recent theoretical study has predicted distinct radical cation dynamics for different glycine conformers; however, no experiment has yet been reported to confirm this prediction.¹⁵

Part 2 of this thesis focuses on understanding conformation specificity for the reactivity of radical cation intermediates of biomolecules. In this effort, conformation

specific and charge directed reactivity of radical cation intermediates of α -substituted bioactive carboxylic acids are first discussed in Chapter 10. Finally, Chapter 11 discusses the possibility of γ -turn specific decomposition of a radical cation intermediate of a small peptide analogue, $\text{CH}_3\text{CO-Gly-NH}_2$, and addresses future direction of the research presented in Part 2 of this thesis.

The radical cations of biomolecules are formed by localization of a hole in the molecules through single photon vacuum-ultraviolet (10.5 eV) photoionization. We show that localization of holes in these radical cations is also conformer-specific. For the unambiguous tracking of a biochemical reaction in a conformation specific way, the isolation and identification of conformations are essential prerequisites, especially for further conformer-selective dynamics studies. With regard to this point, the supersonic jet expansion is used in getting internal temperature low enough ($\sim 3\text{K}$) to suppress the interconversion between different conformers. Once the molecules are trapped in different local minima (conformers) of the PES, we identify each conformer through IR-VUV spectroscopic characterization of its vibrational frequencies. Conformation specific fragmentation patterns of radical cation intermediates are demonstrated by observing different IR spectra (corresponding to different conformers) obtained at different fragment mass channels. These experimental results are interpreted with the aid of *ab initio* calculation with the CASSCF and MP2 methodologies. The calculations reveal characteristics of the low lying doublet cationic PESs of different conformers, different $(D_1/D_0)_{\text{CI}}$ conical intersections, and different location sites of hole, all of which are responsible for the conformer specific reactivity of radical cation intermediates of biomolecules.

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CHAPTER 10

Conformation Specific and Charge Directed Reactivity of Radical Cation

Intermediates of α -substituted (Amino, Hydroxy, and Keto)

Bioactive Carboxylic Acids

Work presented in this chapter is submitted for publication in “Bhattacharya, A.; Shin, J.-W.; Clawson, K.; Bernstein, E. R. *J. Am. Chem. Soc.* **2009**.” I have performed all the experiments and theoretical calculations independently. IR-VUV spectra of glycine and valine were recorded by Yongjun.

10.1 Introduction

Radical cation intermediates of α -substituted carboxylic acid based biological building blocks, such as amino acids, peptides and proteins, lactic acid, and pyruvic acid, have major roles in biochemistry and medicinal chemistry,¹ and are responsible for the development of a wide range of human physiological disorders.^{2,3} In the past few years, the properties of different bioactive carboxylic acid-derived radicals have attracted considerable attention, both from the experimental⁴⁻¹⁰ and theoretical points of view.¹¹⁻²² These reactive intermediates are generated *in vivo* by means of removal of an electron from the parent molecule due to ionizing radiation, oxidative stress, and metal cofactors.^{1(d)} These radical cations can eventually result in enzyme inhibition, and in

denaturation, degradation, and fragmentation of proteins. Therefore, a detailed characterization of the reactivity and stability of radical cationic α -substituted bioactive carboxylic acids is highly desirable and is of great interest in toxicology, pharmacology, and radiation biology.²³

Knowledge of the stability and reactivity of radical cationic bioactive species is also of particular interest for understanding prebiotic chemistry under conditions of the early earth,^{24,25} when the earth was more exposed to vacuum ultraviolet (VUV) ionizing radiation than it is today. At that time, bioactive carboxylic acid based biological building blocks, such as amino acids, lactic acid, pyruvic acid, must have preceded life. Recent evolutionary theory (iron-sulfur world theory)²⁶ for the origins of life posits that, under conditions of the early earth, formation of pyruvic acid, which produces bio-energy through acetyl-CoA in the network of metabolic processes, provided the fertile basis for the formation of life. Thus, understanding the stability and reactivity of bioactive carboxylic acid radical cations can help decipher the natural phenomena that served to protect some of the prebiotic molecules against dissociative damage caused by ionizing radiation under conditions of the early earth.

The location of the charge and hydrogen bonding in a radical cation is of paramount importance for its reactivity and stability.²⁷ One of the most important aspects of the reaction dynamics of radical cation intermediates of peptides involves an extremely rapid (subfemtosecond) transfer of charge²⁸ and alteration of their reactivity due to variation of local sites for ionization.²⁷ Recent theoretical studies have predicted that charge migration in radical cations of glycine, following the ionization of an electron from three different orbitals, strongly depends on specific orientation of the

atoms in the molecule (conformations).²⁹ Such charge migration can lead to distinct reaction dynamics for different glycine conformers;³⁰ however, experiments have not yet confirmed this prediction.

The flexibility of three dimensional structures of α -substituted bioactive carboxylic acids permits great conformational diversity. Different conformers can interconvert *via* hindered rotations about single bonds, giving rise to conformational isomerism. The behavior of these ionized conformers can be governed by their initial detailed molecular structures. Therefore, a detailed characterization of conformation specific reactivity of radical cation intermediates of α -substituted bioactive carboxylic acids would be invaluable for understanding the phenomenon of oxidative stress at a molecular level. A few studies of conformer selective dynamics of isolated radical cation intermediates of α -substituted bioactive carboxylic acids have recently appeared in literature.^{30,31}

For unambiguous tracking of a conformation specific biochemical reaction and its dynamics, isolation and identification of conformations are essential prerequisites. We achieve such an analysis using a supersonic jet expansion to obtain an internal temperature low enough to suppress interconversion between different conformers. Once the conformers are trapped in different local minima of their ground state potential energy surface (PES), conformation specific fragmentation patterns for radical cation intermediates are proven by observing different infrared (IR) spectra (corresponding to different conformers) obtained at different fragment signals generated through the ionization process. The experimental studies are accompanied by highly correlated *ab initio* calculations at the MP2 and CASSCF levels of theory.

Here, we report the remarkable difference in fragmentation behavior among different conformers of radical cationic lactic acid (α -hydroxy acid), pyruvic acid (α -keto acid), and glycine and valine (α -amino acids). The conformation specific differences in reactivity are explained by conformation mediated localization of the positive charge (or hole) on the radical cations formed through single photon vacuum ultraviolet (10.5 eV) ionization. Lactic acid, glycine, and valine undergo complete and conformation directed dissociation following ionization at 10.5 eV. Conformers of these molecules, for which the α -substituent donates a hydrogen bond to the carboxylic acid group, favor either C_{α} - $C_{\text{carboxylic}}$ bond dissociation or hydrogen transfer from the α -substituent to the carboxylic acid group. The hydrogen transfer, however, depends on the activation barrier and the relative orientation of the singly occupied molecular orbital (SOMO, where the charge/hole resides) with respect to the C_{α} - $C_{\text{carboxylic}}$ bond. Conformers for which the α -substituent of these molecules accepts a hydrogen bond from the carboxylic acid OH facilitate hydrogen transfer from the carboxylic acid OH to the α -substituent. Pyruvic acid, on the other hand, does not undergo complete dissociation following ionization, resulting in a stable radical cation. We have identified two different conformers of pyruvic acid, both of which undergo, to some extent, C_{α} - $C_{\text{carboxylic}}$ dissociation; however, the reaction pathways associated with C_{α} - $C_{\text{carboxylic}}$ dissociation for the two conformers have different exothermicities. Thus, the reactivity and stability of radical cationic bioactive carboxylic acids is dependent on the properties of their original conformations. The radical cation of pyruvic acid has a special stability in this respect.

10.2 Experimental Methods

The experimental setup used to record time of flight mass spectra and IR-VUV ionization spectra has been previously described in detail.^{32,33} Lactic acid and pyruvic acid are placed behind the pulsed valve body (Parker General Valve series 9) and are heated to about 50°C to increase their vapor pressure. The gaseous molecules are brought into the molecular beam by a neon/helium gas mixture (69%/31%) at 30 psig backing pressure. After passing through a skimmer, the molecular beam interacts with pulsed VUV and IR laser beams in the ionization region of a time of flight mass spectrometer.

The IR laser beam, which precedes by 50 ns and counterpropagates with respect to the 118 nm laser beam, is focused at the VUV/molecular beam interaction point by a 60 cm focal length lens to probe neutral ground state species. The 118 nm radiation is the ninth harmonic of the fundamental output of a Nd:YAG laser at 1064 nm. 355 nm radiation (third harmonic) of the Nd:YAG laser is focused into a cell with Xe/Ar at a ratio of 1:10 at 330 Torr total pressure. An MgF₂ lens focuses the 118 nm light in the ionization region of the TOFMS and disperses the remaining 355 nm light. The tunable IR laser output generated by an OPO/OPA system (Laser Vision), pumped by 532 nm radiation from another Nd:YAG laser, has an energy of 3-5 mJ/pulse and a bandwidth of ~2 cm⁻¹ in the 2800-3800 cm⁻¹ range.

10.3 Theoretical Methods

For rigorous descriptions of the PES of radical cationic bioactive carboxylic acids, highly correlated multiconfigurational methods, such as CASSCF or CASPT2, are absolutely necessary. These multiconfigurational methodologies are particularly

important for calculating surfaces with “near degeneracy effects” caused by presence of conical intersections between the many low lying valence ion states. Ground electronic surface topology is often found to be altered by proximity of an upper excited electronic state surface along a particular reaction coordinate near a conical intersection, which can only be calculated through multiconfigurational methods. Monoconfigurational methods such as HF or MP2 often overestimate or underestimate the energy barrier to a transition state on the ground electronic surface of the radical ion near conical intersections. Illustrations of such a consideration are found recently for many organic compounds³⁴ and for conformer I of lactic acid and conformer II of glycine and valine. Therefore, in the present work, exploration of cationic PESs is performed using the CASSCF level of theory. MP2 results, however, are given in Figures 10.S2, 10.S3, and 10.S4, in Supplementary Information for comparison.

All geometry optimizations relevant to the ion state decomposition of lactic acid, pyruvic acid, glycine, and valine are carried out at the CASSCF/6-31G(d) and MP2/aug-cc-pVDZ levels of theory using the Gaussian 03³⁵ and MOLPRO³⁶ programs. To explore the ion state PESs, the active space comprises 9 electrons distributed in 8 orbitals, denoted as CASSCF(9,8). The orbitals used in the active space of lactic acid, pyruvic acid, glycine, and valine are illustrated in Figure 10.S1, Supplementary Information. Theoretical estimates of the vertical ionization energies (VIEs) could be performed using an outer-valence Green’s function method; however, here we determine the lowest VIE explicitly calculating the energy difference between neutral and cation at the Franck-Condon geometry employing the MP2/aug-cc-pVDZ level of theory. Critical points (minima and transition states) are characterized by analytical

frequency calculations. Minimum energy paths are calculated using an intrinsic reaction coordinate (IRC) algorithm implemented in the Gaussian 03 program suite. Conical intersection search is also performed using the algorithm implemented in Gaussian 03.

10.4 Experimental Results

Lactic acid: Lactic acid has three internal rotation axes that can give rise to a number of conformational isomers. It also has a chiral carbon which leads to the existence of enantiomers. As IR-VUV photoionization spectroscopy is not sensitive to molecular chirality effects, identification of different enantiomers of lactic acid is not possible using this spectroscopic technique; however, this technique can identify different conformers of lactic acid present in the molecular beam.

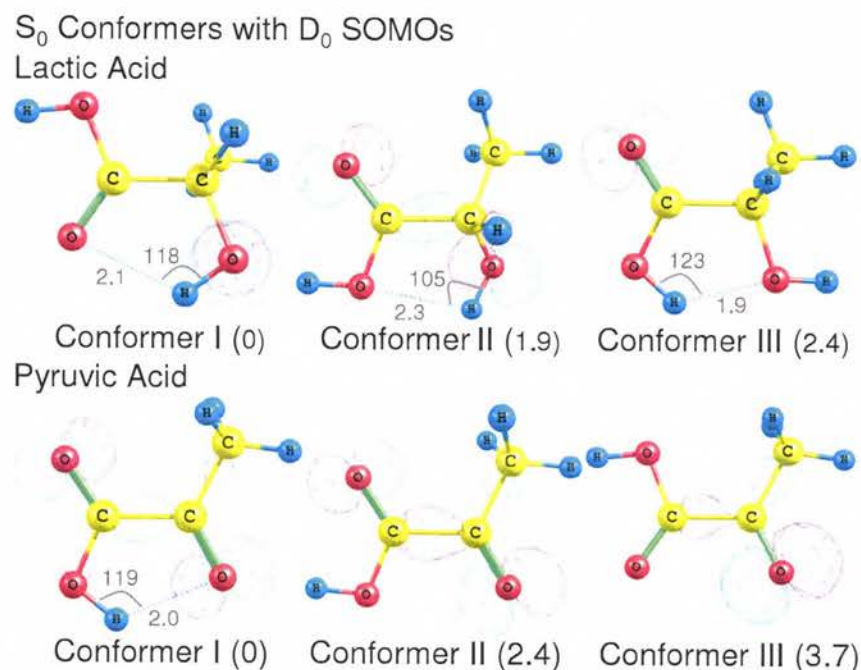


Figure 10.1: The three lowest energy conformers of ground state (S_0) neutral lactic acid and pyruvic acid with calculated (MP2/aug-cc-pVDZ) relative energies (in kcal/mol), showing their bond distances and bond angles. The density plots for the SOMO (singly occupied molecular orbital) of lactic acid and pyruvic acid at the FC (Franck-Condon) point on the cationic D_0 surface calculated at the CASSCF(9,8)/6-31G(d) level of theory are also shown. The two colors for these orbitals indicate the plus and minus phases of the wavefunction.

The three lowest energy conformers of neutral lactic acid with calculated (MP2/aug-cc-pVDZ) relative energies (in kcal/mol) are depicted in Figure 10.1. These results are in agreement with previous theoretical calculations,³⁷ and the available microwave spectroscopy³⁸ and FTIR³⁹ data. The conformers differ mainly by different types of intramolecular hydrogen bonding linkages: O-H $\cdots$ O=C (conformer I), O-H $\cdots$ O(H)CO (conformer II), and C(O)O-H $\cdots$ O-H (conformer III). Conformer I in Figure 10.1 represents the lowest energy conformer. The remaining possible conformers, which are not shown in the figure, are estimated to have a total population of less than 0.1% at 298 K,³⁹ and therefore have been considered of no interest for our present molecular beam study.

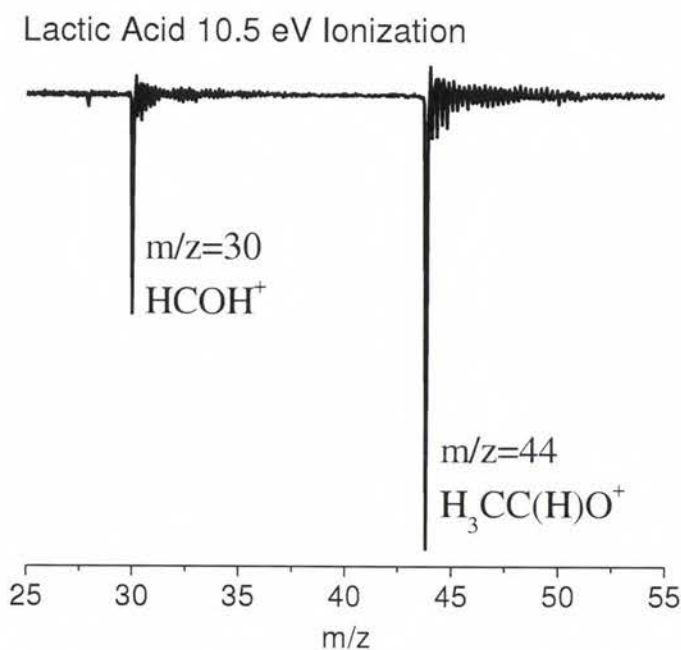


Figure 10.2: Time of flight mass spectrum for lactic acid ionized at 10.5 eV.

Figure 10.2 shows the TOF mass spectrum of lactic acid obtained through single photon ionization at 10.5 eV. The ion signals at $m/z=44$ and 30 amu correspond to

$\text{H}_3\text{CC(H)CO}^+$ and HCOH^+ fragments, respectively. The absence of a parent ion signal indicates that lactic acid undergoes complete molecular fragmentation following single photon vertical ionization at 10.5 eV.

The more intense fragment ion signal at $m/z=44$ amu in the mass spectrum (see Figure 10.2) can be assigned to a product resulting from intramolecular hydrogen transfer from the $\alpha\text{-OH}$ to the COOH group followed by breaking of the $\text{C}_\alpha\text{-C}_{\text{carboxylic}}$ bond from either conformer I or II. This fragment ion signal cannot be generated from conformer III because the hydrogen bond is formed by the carboxylic acid OH group H atom bonding to the $\alpha\text{-OH}$ group. The ion signal at $m/z=30$ amu can be attributed to a product formed upon direct $\text{C}_\alpha\text{-C}_{\text{carboxylic}}$ bond dissociation followed by elimination of the CH_3 radical from all three lowest energy conformers of lactic acid. Therefore, with the diversity of different possible fragmentation pathways for each conformer, the TOFMS alone does not enable us to unambiguously identify the fragmentation patterns of the radical cation intermediates of lactic acid in a conformation specific way. For further study of the conformer selective dynamics of radical cation lactic acid, the identification of the conformer involved in a specific fragmentation reaction is essential. This identification can be performed using IR-VUV photoionization spectroscopy.

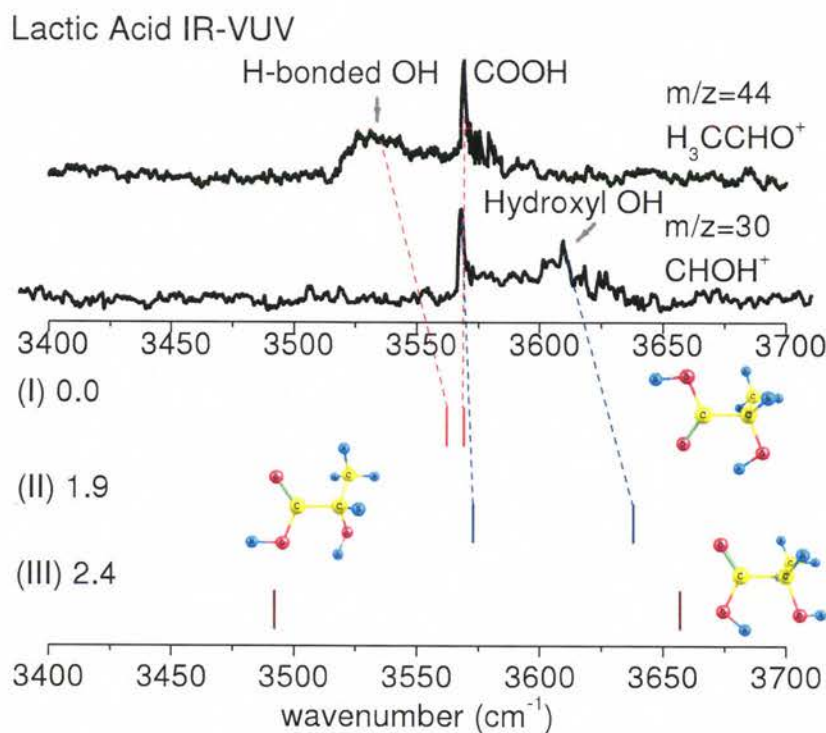


Figure 10.3: IR-VUV spectra of lactic acid recorded monitoring fragment signals at $m/z=44$ and 30 amu in the region of free or hydrogen bonded OH stretching modes. Colored vertical bars represents calculated (MP2/aug-cc-pVDZ), scaled (0.96), harmonic frequencies for the different conformers of lactic acid. For conformer I, the left vertical bar indicates the hydrogen bonded OH stretch. For conformer II, the right vertical bar indicates hydrogen bonded OH stretch.

The infrared spectra of lactic acid recorded monitoring the fragment signals at $m/z=44$ and 30 amu using IR-VUV spectroscopy is illustrated in Figure 10.3. Enhancement of the ion signal intensity is observed at both fragment mass channels when the IR radiation is absorbed by a characteristic normal mode of vibration for a specific conformer of lactic acid. Several calculated (MP2/aug-cc-pVDZ) scaled (0.96) harmonic vibrational frequencies are also displayed in Figure 10.3 below the experimental spectra, each of which is specific to a given conformer of lactic acid. The IR spectra obtained at fragment mass channels of $m/z=44$ and 30 amu, illustrated in

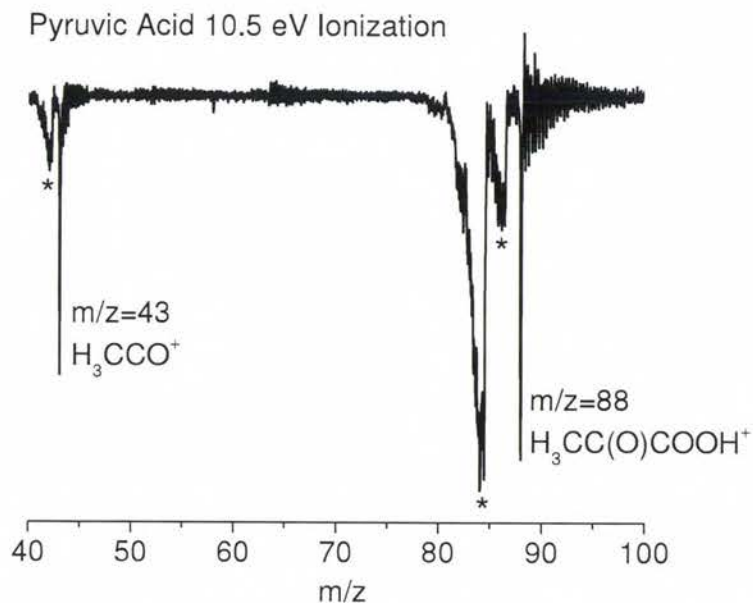
Figure 10.3, are in good agreement with the scaled (0.96) harmonic calculated IR frequencies of conformers I and II, respectively.

A qualitative assignment of the IR spectra can easily be derived from the sensitivity of the OH stretch vibration to the environment of the OH bond; in particular, its involvement in a hydrogen bond. Hydrogen bonding in the molecular system is responsible for the red-shift ($100\text{--}300\text{ cm}^{-1}$ depending on the strength of H-bond) in the ν_{OH} stretch vibrational frequency compared to the free (non-hydrogen bonded) OH stretching mode.⁴⁰ Absorption of an OH stretching mode associated with a hydrogen bonded OH moiety is also often broadened due to complex anharmonic coupling mechanism involving normal modes associated with the $\text{O-H}\cdots\text{O}$ hydrogen bond forming atoms and other overtone and combination modes.⁴¹

The above considerations are clearly pertinent for the spectra in Figure 10.3. The sharp peaks corresponding to the free carboxylic acid OH stretch (appears near 3569 cm^{-1}) are observed in both spectra. A broad feature appears to the red of the free carboxylic acid OH stretch in the IR spectrum obtained at the fragment mass channel of $m/z=44$ amu; this feature can be assigned as the hydrogen bonded hydroxyl OH stretch. A sharp feature appears to the blue of the free carboxylic acid OH stretch in the IR spectrum recorded at the fragment mass channel of $m/z=30$ amu; this feature can be attributed to the free hydroxyl OH stretch. The relative positions of hydroxyl OH stretching mode (either hydrogen bonded or free) in the two spectra provide qualitative information about the relative strength of $\text{O-H}\cdots\text{O}$ intramolecular interaction for conformers I and II. The larger red-shift of the hydroxyl OH oscillator of conformer I confirms that this conformer possesses a strong $\text{O-H}\cdots\text{O}$ hydrogen bond interaction.

Absence of a strongly red-shifted hydroxyl OH oscillator in conformer II corroborates a weak van der Waal interaction between α -hydroxy OH and COOH group. The mismatch between experimental and theoretical results for hydrogen bonded or free hydroxyl OH frequencies in the spectra presumably arises due to strong anharmonic coupling and coupling between the harmonic frequency mode and low frequency combination modes, which are not considered in the calculation at MP2/aug-cc-pVDZ level of theory. The qualitative observation of a red-shift of more than 130 cm^{-1} associated with the hydrogen bonding effect for conformer I is, however, well reproduced in the calculation. Furthermore, since a free hydroxyl OH stretch frequency is observed at 3610 cm^{-1} monitoring the fragment signal at $m/z=30$ amu, conformer I has no contribution to the ion signal at $m/z=30$ amu. No hydrogen bonded carboxylic acid OH stretch frequency is observed in either of these spectra; thus the conformer III does not contribute to either the fragment signal at $m/z=44$ or 30 amu. Instead, these two fragments at mass channels $m/z=44$ and 30 amu come entirely from conformers I and II, respectively.

Pyruvic acid: Figure 10.1 depicts the three lowest energy conformers of neutral pyruvic acid with the calculated (MP2/aug-cc-pVDZ) relative energies (in kcal/mol). They differ by the type of hydrogen bonding, and relative orientation of the α -keto group with respect to the COOH group. Conformer I in Figure 10.1 is the lowest energy conformer, which is in agreement with the literature.⁴²



*Figure 10.4: Time of flight mass spectrum for pyruvic acid ionized at 10.5 eV. The ion signals denoted by * are due to diffusion pump oil which was present in the vacuum chamber.*

The TOF mass spectrum of pyruvic acid obtained using single photon ionization at 10.5 eV is depicted in Figure 10.4. The spectrum contains a parent ion signal at $m/z=88$ amu and one fragment signal, corresponding to H_3CCO^+ , at $m/z=43$ amu. The fragment ion signal at $m/z=43$ amu can be attributed to a product resulting from direct $\text{C}_\alpha\text{-C}_{\text{carboxylic}}$ bond dissociation from all three low energy conformers (Figure 10.1). Further identification of the different conformers contributing to the direct $\text{C}_\alpha\text{-C}_{\text{carboxylic}}$ bond dissociation channel is performed using IR-VUV photoionization spectroscopy.

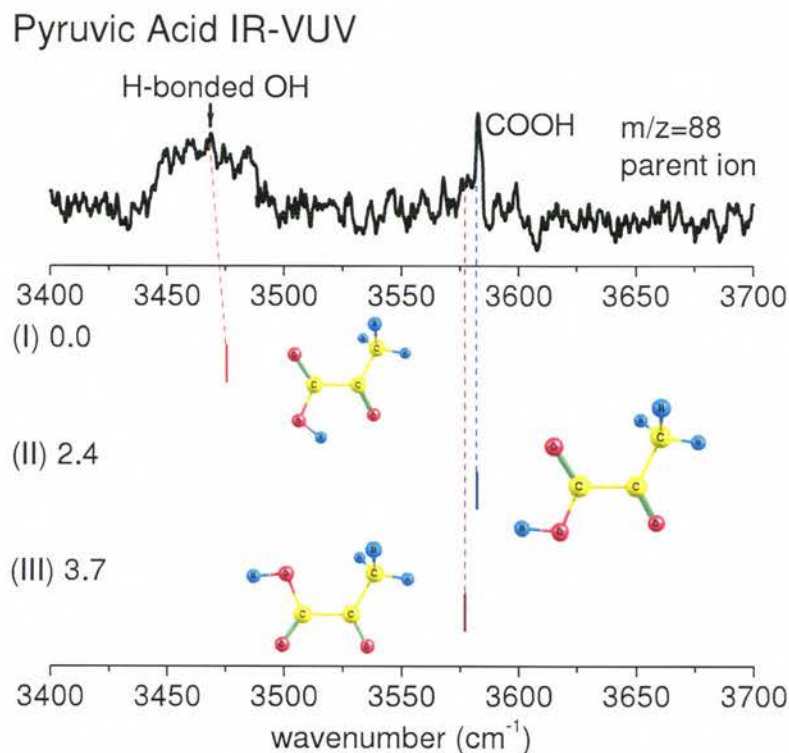


Figure 10.5: IR-VUV spectra of pyruvic acid recorded monitoring the parent ion signal at $m/z=88$ amu in the region of free or hydrogen bonded OH stretching modes. Colored vertical bars represents calculated (MP2/aug-cc-pVDZ), scaled (0.96), harmonic frequencies for the different conformers of pyruvic acid.

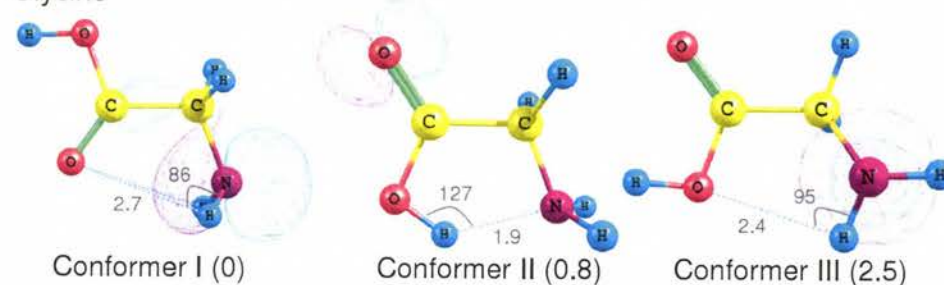
The infrared spectrum, obtained by monitoring the pyruvic acid parent ion signal at $m/z=88$ amu, is given in Figure 10.5. No IR spectrum could be recorded monitoring the fragment signal at $m/z=43$ amu. An enhancement in ion signal intensity is observed at the mass channel $m/z=88$ amu when the IR radiation is absorbed by the specific normal mode of vibration for a particular conformer of pyruvic acid. Enhancement of the parent ion signal intensity in the presence of IR radiation arises due to the enhancement in ionization cross section of the parent molecule from its vibrationally excited states. The IR spectrum in Figure 10.5 is comprised of two features resulting from the two different environments of the carboxylic acid OH bond:

one is associated with the free OH stretch (3582 cm^{-1}) and other is associated with the hydrogen bonded carboxylic acid OH stretch (3460 cm^{-1}). The sharp feature in the spectrum at 3582 cm^{-1} exhibits an excellent fit with the calculated IR frequency of the free carboxylic acid OH stretch for conformer II and III, which is also in good agreement with recent FTIR measurements.⁴³ The broad feature to the red of the free OH stretch in the spectrum can be ascribed to a hydrogen bonded carboxylic OH stretch, which is qualitatively consistent with the calculated vibrational frequency of hydrogen bonded carboxylic acid OH stretch for conformer I. The free carboxylic acid OH stretch observed at 3582 cm^{-1} is also in agreement with the calculated vibrational frequency for the conformer III; however, this conformer is estimated to have total population less than 0.2% at 300 K using a Boltzmann population distribution, and therefore, has been considered to contribute little to our present study. We can, thus, conclude that both conformers I and II are present in the molecular beam. The only fragment signal observed following single photon ionization of pyruvic acid at 10.5 eV corresponds to H_3CCO^+ , at $m/z=43$ amu; in principle, it can be generated from both of these two conformers. The fragmentation mechanism will be further explored using theoretical calculations.

Glycine and valine: To probe conformation-specificity in the reactivity of radical cationic glycine and valine we reillustrate here the results for these two molecules that were previously experimentally examined by Hu, *et al.*⁴⁴ Being close in spirit to the previous demonstration, the present effort reexamines some of those results to assess conformation-specificity in the reactivity of radical cationic glycine and valine.

S_0 Conformers with D_0 SOMOs

Glycine



Valine

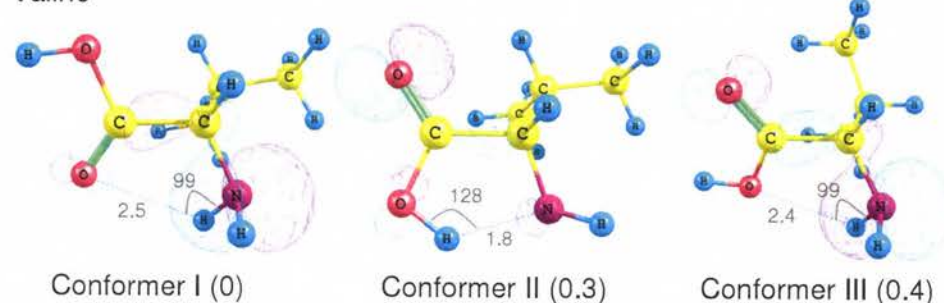


Figure 10.6: The three lowest energy conformers of ground state (S_0) neutral glycine and valine with calculated (MP2/aug-cc-pVDZ) relative energies (in kcal/mol), showing their bond distances and bond angles. The density plots for the SOMO (singly occupied molecular orbital) of glycine and valine at the FC (Franck-Condon) point on the cationic D_0 surface calculated at the CASSCF(9,8)/6-31G(d) level of theory are also shown. The two colors for these orbitals indicate the plus and minus phases of the wavefunction.

Three lowest energy conformers of neutral glycine and valine, which differ again mainly by different types of intramolecular hydrogen bonding linkages, are illustrated in Figure 10.6. Single photon ionization of glycine at 10.5 eV reveals two important fragment signals at $m/z=30$ and 31 amu along with the other weaker fragment signals at $m/z=42$ and 43 amu.⁴⁴ The fragment signal at $m/z=30$ amu (corresponds to $H_2CNH_2^+$) can be attributed to a product formed upon direct C_α - $C_{\text{carboxylic}}$ bond dissociation from all three conformers of glycine. The fragment signal at $m/z=31$ amu (corresponds to $H_2CNH_3^+$) can be assigned to a product formed upon hydrogen transfer from the COOH to the α - NH_2 group followed by C_α - $C_{\text{carboxylic}}$ bond dissociation. No IR

spectra could be recorded monitoring the fragment signal at $m/z=31$ amu; however, in the original study,⁴⁴ an IR spectrum is obtained monitoring the fragment signal at 30 amu, which is reproduced in Figure 10.7.

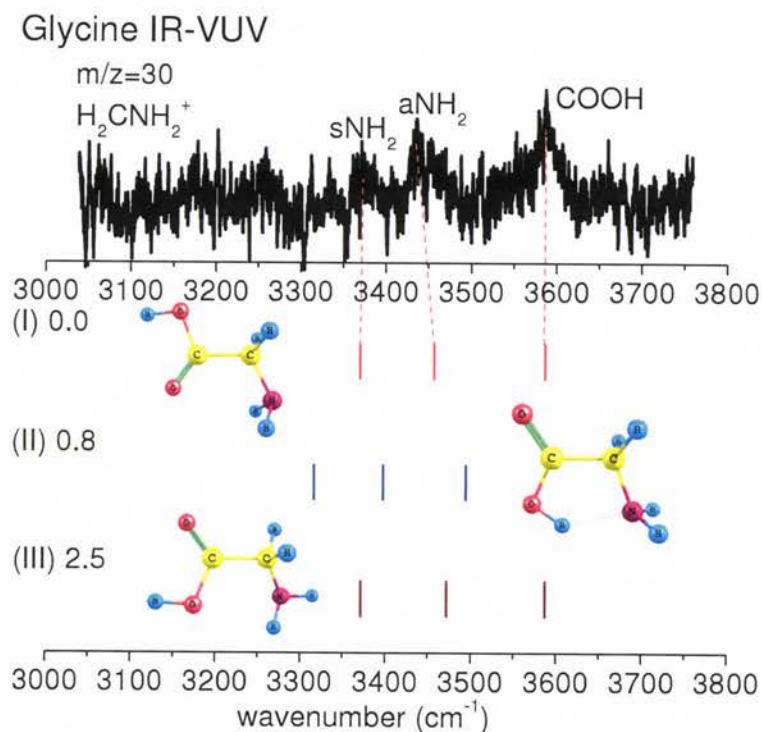


Figure 10.7: IR-VUV spectra of glycine recorded monitoring the fragment ion signal at $m/z=30$ amu in the region of free or hydrogen bonded OH stretching mode and NH_2 stretching mode. Colored vertical bars represents calculated (MP2/aug-cc-pVDZ), scaled (0.96), harmonic frequencies for the different conformers of glycine. The IR spectrum is reproduced from Ref. 44.

The IR spectrum reveals three distinct features that arise due to free symmetric (at 3360 cm^{-1}) and asymmetric (at 3440 cm^{-1}) NH_2 stretches and a free carboxylic acid OH stretch (at 3587 cm^{-1}). This assignment is consistent with the calculated scaled harmonic vibrational frequencies for conformers I and III of glycine. No hydrogen bonded carboxylic acid OH stretch is observed in the IR spectrum obtained at ion signal of $m/z=30$ amu, which indicates that the fragment H_2CNH_2^+ is not generated from

conformer II through C_{α} - $C_{\text{carboxylic}}$ bond dissociation. Only conformer I and III, instead, follow the C_{α} - $C_{\text{carboxylic}}$ bond dissociation pathway.

The fragment signal at $m/z=31$ amu (corresponds to $H_2CNH_3^+$) is unique with regard to the possible fragmentation mechanism of glycine radical cation because it can only be generated from conformer II through hydrogen transfer from the COOH group to the α - NH_2 group followed by C_{α} - $C_{\text{carboxylic}}$ bond dissociation. This argument can adequately be used to corroborate the assignment that the fragment $CH_2NH_3^+$ results from conformer II. This assignment is, however, experimentally demonstrated using an equivalent fragment signal of valine obtained at $m/z=73$ amu (corresponding to $(CH_3)_2C(H)C(H)NH_3^+$).⁴⁴

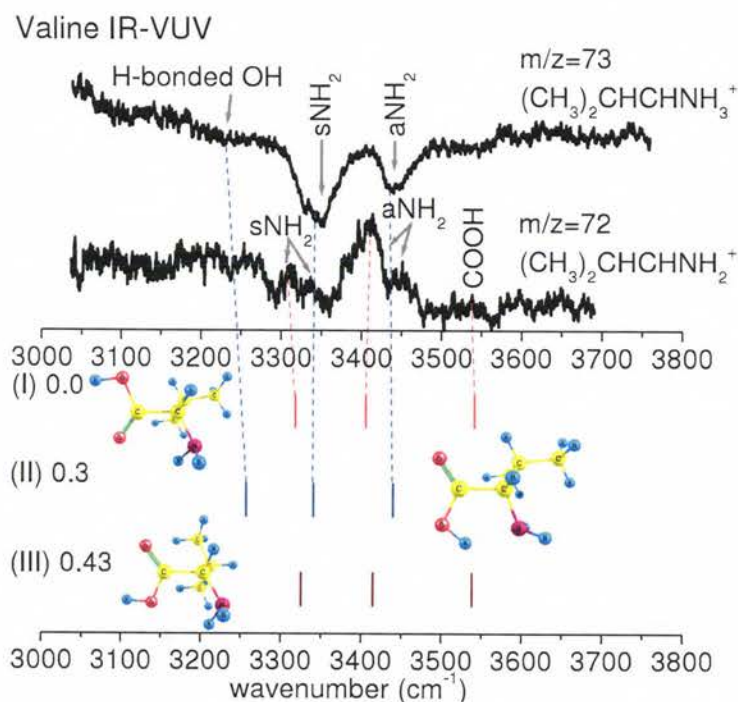


Figure 10.8: IR-VUV spectra of valine recorded monitoring the fragment signal at $m/z=72$ and 73 amu in the region of OH and NH_2 stretching modes. Colored vertical bars represents calculated (MP2/aug-cc-pVDZ), scaled (0.96), harmonic frequencies for different conformers of valine. The IR spectra are reproduced from Ref. 44.

Single photon ionization of valine at 10.5 eV exhibits several important fragment signals at $m/z=73$, 30, and 72 amu.⁴⁴ The fragment signal at $m/z=73$ amu can be related to a product formed upon hydrogen transfer from COOH to the α -NH₂ group followed by C _{α} -C_{carboxylic} bond dissociation. The IR spectra (see Figure 10.8) obtained at this fragment mass channel (negative) clearly reveals a broad feature below 3300 cm⁻¹, corresponding to a hydrogen bonded carboxylic acid OH stretch, and two distinguishable bands, which arise from free symmetric (at 3346 cm⁻¹) and asymmetric (at 3436 cm⁻¹) NH₂ stretches. This assignment is also in good agreement with the calculated scaled harmonic vibrational frequencies for conformer II of valine. The noticeable broadening of each feature associated with symmetric and asymmetric NH₂ stretching modes in the spectrum possibly arises from almost free rotation of the isopropyl group along the C _{α} -C _{β} bond in valine, which renders two additional conformers each retaining the hydrogen bonded network in the α -amino carboxylic acid moiety or retaining possible interactions between the NH₂ and OH moieties. The negative signal at mass channel $m/z=73$ amu is discussed in ref. 44.

The fragment signal at 72 amu can be related to the direct C _{α} -C_{carboxylic} bond dissociation pathway for all three conformers of valine. The IR spectrum (see Figure 10.8) obtained monitoring this fragment signal shows one hydrogen bonded NH stretch (at 3309 cm⁻¹) and one free NH stretch (at 3409 cm⁻¹); the position of each feature is clearly different from that obtained at the fragment mass channel $m/z=73$ amu. The IR spectrum obtained monitoring the fragment signal at $m/z=72$ amu is also in good agreement with the calculated scaled vibrational frequencies for conformer I. In addition, each spectral feature obtained monitoring the fragment signal at $m/z=72$ amu

is associated with a weak shoulder (see Figure 10.8), the position of which is slightly blue to the more intense feature. The shoulder peaks are in good agreement with the calculated scaled vibrational frequencies of free and hydrogen bonded NH stretches for conformer III.

Thus, conformers I and II of both radical cationic glycine and valine dissociate through two distinctly different decomposition pathways. Conformer I undergoes direct C_{α} - $C_{\text{carboxylic}}$ bond dissociation, whereas conformer II undergoes hydrogen transfer followed by C_{α} - $C_{\text{carboxylic}}$ bond dissociation. Thus radical cationic reactivity of glycine and valine, which are α -amino aliphatic carboxylic acids, is conformation specific. Conformer III for glycine and valine, similar to conformer I of these two compounds, however, follows direct C_{α} - $C_{\text{carboxylic}}$ bond dissociation pathway.

10.5 Theoretical Results

Specific knowledge of the molecular ion state produced upon sudden removal of an electron (obeying the Franck-Condon principle) from a molecule is essential in order to determine the likely fragmentation mechanisms of the nascent radical cation. The photoelectron spectrum of the neutral parent molecule can explicitly document the ion states generated by vertical ionization of bioactive carboxylic acids;⁴⁵ however, here we determine relevant molecular ion states produced by vertical ionization at 10.5 eV from comparison between the computed (at MP2/aug-cc-pVDZ) VIE and the experimental ionization energy (10.5 eV). A detailed presentation of this comparison can be found in Table 10.T1 of Supplementary Information. This comparison and the available photoelectron spectra⁴⁵ indicate that ionization of lactic acid, pyruvic acid, glycine, and

valine at 10.5 eV efficiently populates only the ground doublet molecular (radical cation) ion state (D_0).

In the one-electron model (Koopmans' theorem),⁴⁶ removal of an electron from a neutral molecule creates a hole in the molecular electronic distribution, that resides at the singly occupied molecular orbital (SOMO) of the nascent radical cation. The SOMO, therefore, represents the electronic character of the nascent molecular cation, which specifies the potential energy landscape for the cation. The densities for the SOMO of the three different conformers of lactic acid and pyruvic acid at the vertical point (Franck-Condon point) on the D_0 surface, computed at CASSCF(9,8)/6-31G(d) level of theory, are shown in Figure 10.1. The two colors indicate the plus and minus phases of the wavefunction. For conformer I of lactic acid, the SOMO is entirely localized on the α -hydroxy O atom (np_O) of the molecular ion, which is notably perpendicular to the C_α - $C_{\text{carboxylic}}$ σ bond. For conformer II, the SOMO is delocalized over the nonbonding orbitals of α -hydroxy O (np_O), carbonyl O ($n\sigma_O$), and the C_α - $C_{\text{carboxylic}}$ σ bond. Furthermore, the np_O of α -hydroxyl O atom in conformer II is almost parallel to the C_α - $C_{\text{carboxylic}}$ bond. For conformer III of lactic acid, on the other hand, the SOMO is entirely localized on the carbonyl O atom ($n\sigma_O$). Therefore, localization sites of the hole in the nascent, Franck-Condon, vertical radical cation of lactic acid on the D_0 surface are clearly conformation specific.

For both conformers I and II of pyruvic acid, the SOMO is delocalized over the non-bonding orbitals of α -carbonyl O atom, carboxylic acid carbonyl O atom, and the C_α - $C_{\text{carboxylic}}$ σ bond with predominant contribution from α -carbonyl O atom. For conformer III, the SOMO is localized primarily on the α -carbonyl O atom of the radical

cation. Additionally, the np_O of the α -carbonyl oxygen atom is parallel to the C_α - $C_{\text{carboxylic}}$ bond for all three conformers of pyruvic acid. Therefore, contrary to the lactic acid conformers, localization site of the hole in the nascent radical cation of pyruvic acid on the D_0 surface is not entirely conformer dependent.

The density for the SOMO of the different vertical ion conformers of glycine and valine on their D_0 ion surface computed at CASSCF(9,8)/6-31G(d) level of theory are shown in Figure 10.6. For conformers I and III of glycine and valine, the SOMO is located on the α -amine N (np_N) of the molecular Franck-Condon ion. For glycine, the np_N in conformer I is parallel to the C_α - $C_{\text{carboxylic}}$ bond and that in conformer III is perpendicular to the C_α - $C_{\text{carboxylic}}$ bond. Both conformers I and III of valine, however, have np_N parallel to the C_α - $C_{\text{carboxylic}}$ bond. For conformer II of glycine and valine the SOMO, on the other hand, is primarily localized on the carbonyl O atom of the molecular ion. These assignments for the SOMO of α -amino carboxylic acids are in good agreement with what has been recently suggested for structurally similar alanine radical cation by Powis, et al.⁴⁷ Therefore, the localization site for the hole of conformer I and II of glycine and valine in D_0 state is clearly conformation specific.

Following sudden removal of an electron from a molecule, the nascent radical cation is typically not formed in its equilibrium geometry. On the femtosecond time scale, the vertical ion will evolve to the adiabatic ion while lowering its electronic energy by adopting a different nuclear arrangement. The excess energy ($E_{\text{VIE}} - E_{\text{AIE}}$) due to vertical-to-adiabatic evolution is stored in the vibration of the bonds of the molecular ion under isolated conditions; this vibrational energy can often cause the dissociation of the radical cation. In some cases, following vertical to adiabatic evolution of the ion,

hydrogen transfer provides additional excess energy ($E_{\text{VIE}} - E_{\text{AIE}} + \Delta H_{\text{reaction}}$) to surmount the energy barrier for molecular dissociation.

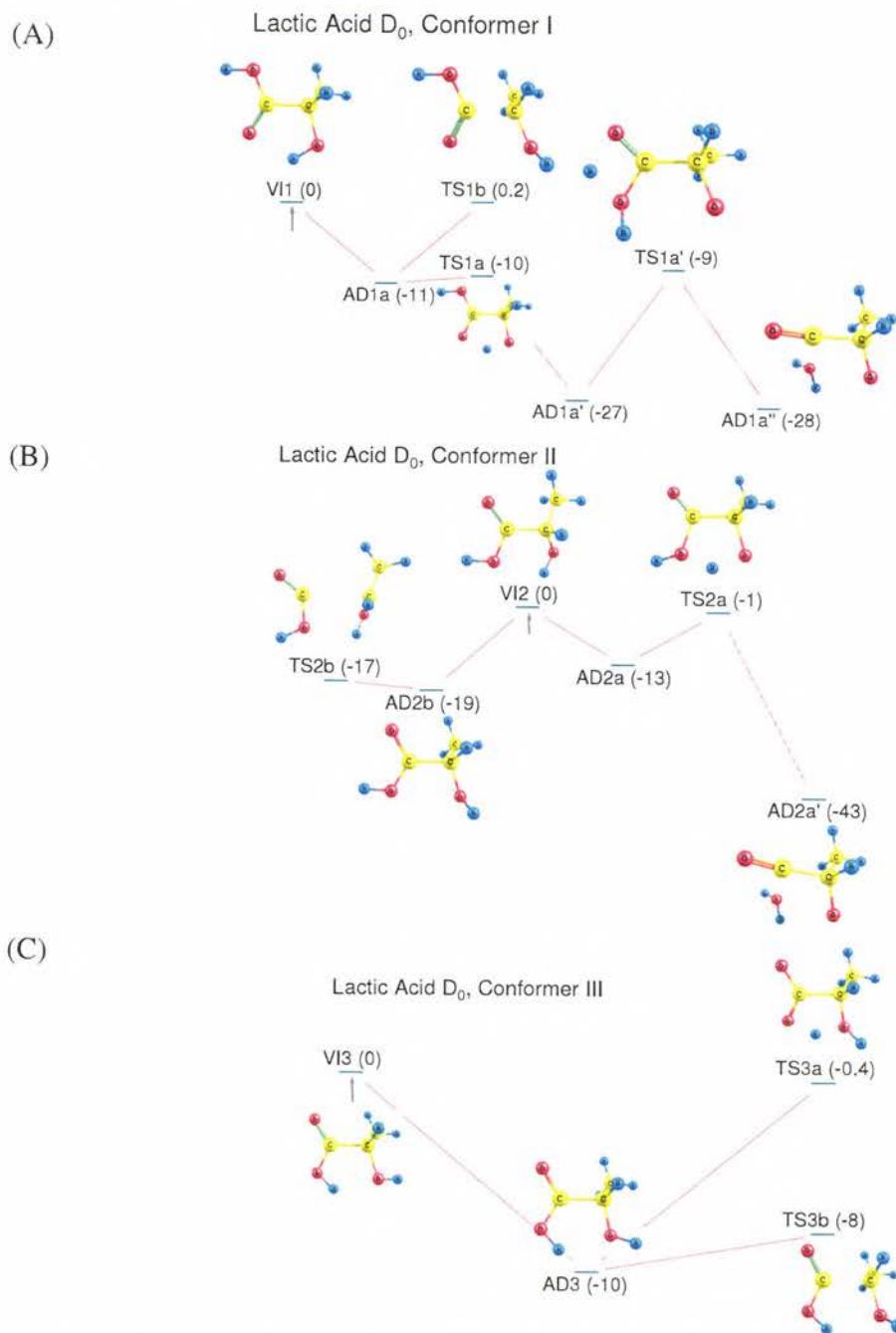


Figure 10.9. Potential energy diagram for lactic acid on its D_0 ion surface calculated at the CASSCF(9,8)/6-31G(d) level of theory. Two decomposition pathways are shown: a) hydrogen transfer, and b) direct C_{α} - $C_{\text{carboxylic}}$ bond dissociation. Relative energies are in kcal/mol. Vertical arrows show the accessed FC point for the ion.

The product distributions observed through mass spectrometry following single photon VUV (10.5 eV) ionization of α -substituted bioactive aliphatic carboxylic acids indicate that the initial step in the decomposition of their radical cation intermediates involves two common mechanisms: (1) hydrogen transfer (either from the carboxylic acid group to the α -substituent or vice versa); and (2) direct C_{α} - $C_{\text{carboxylic}}$ bond dissociation. Therefore, we consider below the theoretical exploration of these two channels of decomposition in order to judge which of them is energetically or dynamically more favorable for a particular conformer.

The potential energy diagrams along the two reaction pathways (hydrogen transfer and COOH elimination) for different conformers of radical cationic lactic acid, pyruvic acid, glycine, and valine on the D_0 surface obtained at the CASSCF(9,8)/6-31G(d) level of theory, are shown in Figure 10.9, 10.10, 10.11, and 10.12, respectively. The hydrogen transfer pathway is indicated by adding a suffix 'a' and C_{α} - $C_{\text{carboxylic}}$ bond dissociation pathway is referred including a suffix 'b' in the aforementioned figures. Here the CASSCF results are presented because they provide a more realistic theoretical picture of the molecular ion states than do the MP2 results (see Figures 10.S2-S4 in Supplementary Information).

The potential energy diagram of lactic acid on D_0 ion surface (see Figure 10.9) reveals that the direct C_{α} - $C_{\text{carboxylic}}$ bond dissociation pathway is the minimum energy pathway (associated with the lowest activation barrier) for conformers II and III. Therefore, these two conformers will lead to a predominately kinetically controlled product at low temperature through this dissociation channel. C_{α} - $C_{\text{carboxylic}}$ bond dissociation pathway possesses, however, different exothermicities for these two

conformers (-17 kcal/mol for conformer II and -8 kcal/mol for conformer III). The hydrogen transfer pathway (from α -OH to COOH), on the other hand, is computed to be the minimum energy pathway for conformer I of lactic acid.

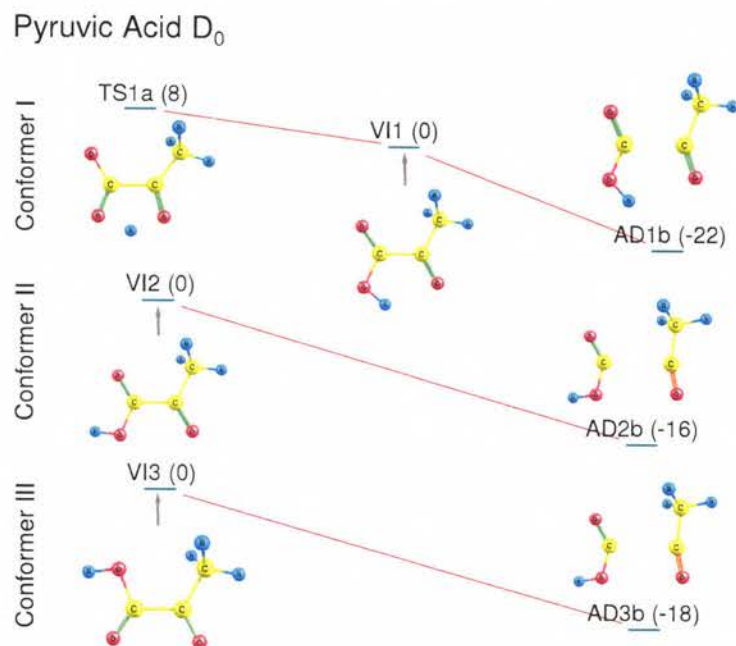


Figure 10.10: Potential energy diagram for pyruvic acid on its D_0 ion surface calculated at the CASSCF(9,8)/6-31G(d) level of theory. Two decomposition pathways are shown: a) hydrogen transfer, and b) direct C_α - $C_{\text{carboxylic}}$ bond dissociation. Relative energies are in kcal/mol. Vertical arrows show the accessed FC point for the ion.

The potential energy diagram of pyruvic acid on the D_0 ion surface (see Figure 10.10) indicates that only C_α - $C_{\text{carboxylic}}$ bond dissociation is the minimum energy pathway for all three conformers of pyruvic acid. A zero activation barrier exists in this reaction coordinate for all three conformers. The computed activation barrier from the FC point on the D_0 surface of pyruvic acid, gives hydrogen transfer from COOH to the α -keto substituent, on the other hand, as a highly endothermic process (by 8 kcal/mol at

the CASSCF level and 21 kcal/mol at the MP2 level). Therefore, hydrogen transfer for this cation should not (and does not) occur for conformer I (see Figure 10.10).

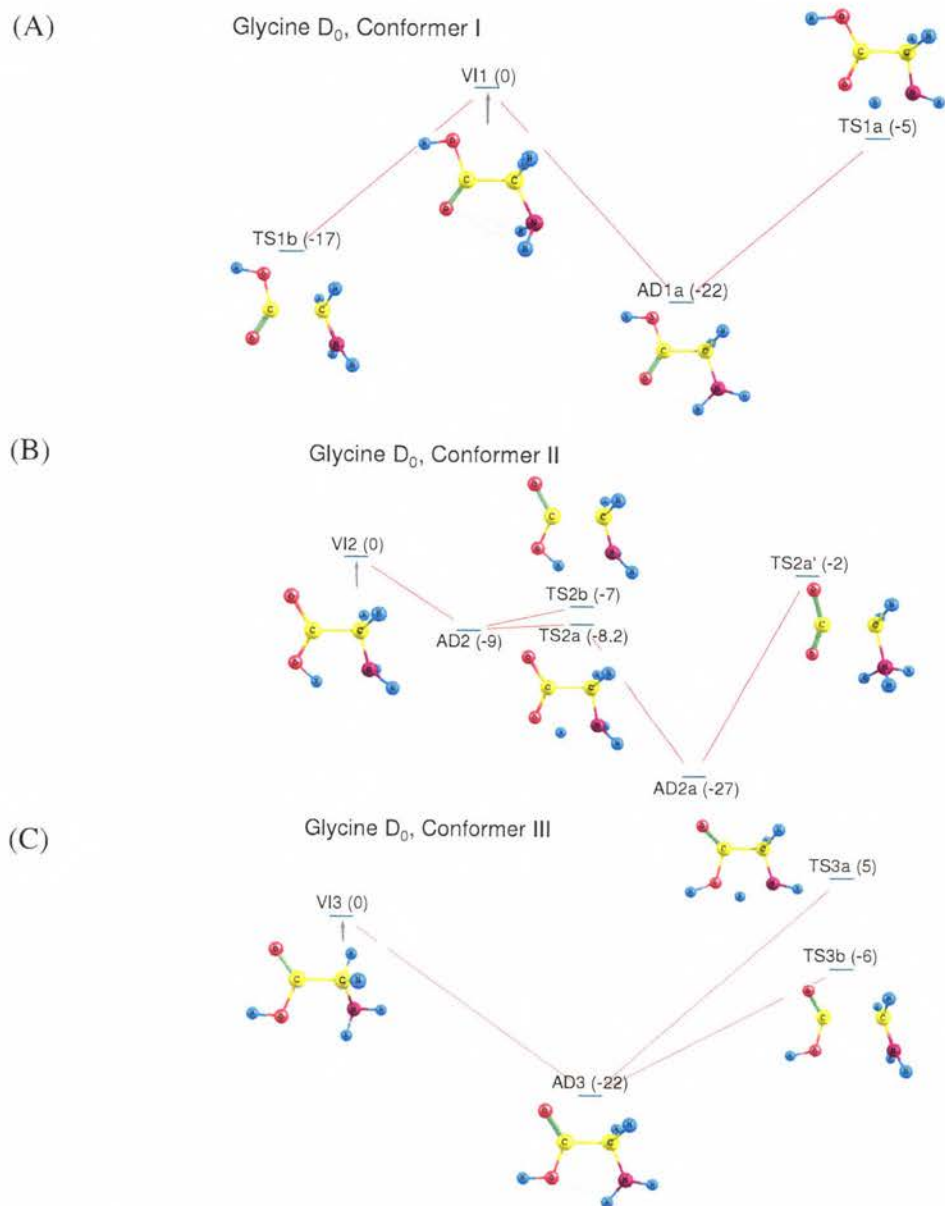


Figure 10.11: Potential energy diagram for glycine on its D_0 ion surface calculated at the CASSCF(9,8)/6-31G(d) level of theory. Two decomposition pathways are shown: a) hydrogen transfer, and b) direct C_α - $C_{\text{carboxylic}}$ bond dissociation. Relative energies are in kcal/mol. Vertical arrows show the accessed FC point for the ion.

The potential energy diagram for glycine on the D_0 surface (see Figure 10.11) shows that C_α - $C_{\text{carboxylic}}$ bond dissociation is the minimum energy pathway for conformers I and III. This reaction coordinate possesses a zero activation energy for conformer I and an activation energy of 16 kcal/mol for conformer III. The hydrogen transfer pathway, however, is the minimum energy pathway for conformer II of glycine. A zero activation energy barrier exists in the C_α - $C_{\text{carboxylic}}$ bond dissociation pathway for conformers I and III of valine (see figure 10.12). The hydrogen transfer pathway for valine is calculated to be the minimum energy pathway for conformer II.

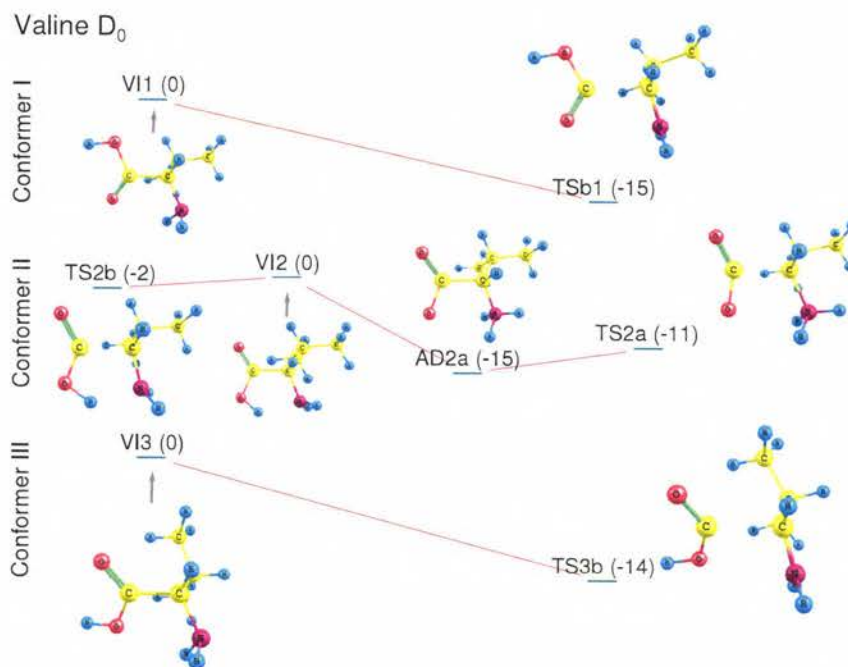


Figure 10.12: Potential energy diagram for valine on its D_0 ion surface calculated at the CASSCF(9,8)/6-31G(d) level of theory. Two decomposition pathways are shown: a) hydrogen transfer, and b) direct C_α - $C_{\text{carboxylic}}$ bond dissociation. Relative energies are in kcal/mol. Vertical arrows show the accessed FC point for the ion.

Thus, the theoretical results show that initial structures of the bioactive carboxylic acids have significant influence on their subsequent reactivity following

ionization. Intramolecular hydrogen bonding can alter the local charge distribution in these radical cation intermediates. Moreover, a relationship between charge, structure, and reactivity emerges from this study. If charge is localized on the carboxylic acid group, hydrogen transfer is favored from COOH to the α -substituent. If the charge is localized on the α -substituent and the SOMO is parallel to the C_{α} - $C_{\text{carboxylic}}$ bond, a charge transfer occurs to the C_{α} - $C_{\text{carboxylic}}$ bond, facilitating direct C_{α} - $C_{\text{carboxylic}}$ bond dissociation without any activation energy barrier. These theoretical findings fully corroborate the experimental observations.

10.6 Discussion

A number of observations are crucial for understanding the conformation specific reactivity of radical cation intermediates of α -substituted bioactive carboxylic acids. Undoubtedly, if the excess energy, obtained through the vertical to adiabatic evolution of the molecular ion, is enough to surmount the activation energy needed to initiate a decomposition reaction, fragmentation of radical cation intermediates takes place. This excess energy may also result in the interconversion between different cation conformations. The interconversion energy for lactic acid, pyruvic acid, glycine, and valine on their ground cation surface is computed to be within the range of 2-6 kcal/mol, which is much smaller than the available excess energy (ranges from 10 to 20 kcal/mol) stored in the molecular vibrations following vertical ionization. Therefore, identical products could possibly be generated from different conformers through interconversion following ionization, which can diminish conformation specific behavior. This consideration, however, can be ruled out: the significant difference in IR spectra (see Figures 10.3 and 10.8 for lactic acid and valine, respectively) recorded

monitoring the fragment signals does not suggest such an interconversion. The IR spectra recorded at different fragment signals are distinctly different and do not appear to be the superposition of two or more components. This suggests that VUV photoionization does not induce the interconversion of the radical cation intermediates of bioactive carboxylic acids. Instead, different conformers move along different reaction pathways following ionization. Thus, the vertical to adiabatic evolution and subsequent fragmentation are faster than the conformational interconversion. The fragmentation dynamics of radical cation intermediates of the bioactive carboxylic acids studied in the present work is predicted to be ultrafast so that each molecule retains the memory of its original conformation.

The theoretical results demonstrate that the direct C_{α} - $C_{\text{carboxylic}}$ bond dissociation channel requires a structural orientation so that the SOMO (usually a nonbonding p-orbital) on the α -substituent stays parallel to the C_{α} - $C_{\text{carboxylic}}$ σ bond (for TS1b, AD2b, and TS3b of lactic acid in Figure 10.9; TS1b, TS3b of glycine in Figure 10.11; TS1b, TS3b of valine in Figure 10.12). This suitable geometrical orientation facilitates hole migration from $2p_O$ (SOMO) to the C_{α} - $C_{\text{carboxylic}}$ σ bond. This charge migration (or hole transfer) initiates direct C_{α} - $C_{\text{carboxylic}}$ bond dissociation because the bond that breaks is the one to which the hole is finally localized in the radical cation. Conformers that have the SOMO localized on the α -substituent and parallel to the C_{α} - $C_{\text{carboxylic}}$ bond at the FC point on the cationic surface, can undergo ultrafast (expected to be on attosecond time scale)^{25,26} charge migration from the α -substituent to the C_{α} - $C_{\text{carboxylic}}$ bond and can thereby generate direct COOH elimination products. Such conformers include conformer II of lactic acid, all three conformers of pyruvic acid, conformer I of glycine,

and conformers I and III of valine. All these conformers require no activation energy for the C_{α} - $C_{\text{carboxylic}}$ bond dissociation reaction pathway from the FC point on the D_0 surface (see Figure 10.9-10.12).

Conformers for which the SOMO is localized on the α -substituent and for which a structural rearrangement is required to make the SOMO parallel to the C_{α} - $C_{\text{carboxylic}}$ bond possess a finite activation barrier for the C_{α} - $C_{\text{carboxylic}}$ bond dissociation. This mechanism is exemplified by conformer I of lactic acid and conformer III of glycine. Conformers for which the SOMO is localized on the carboxylic acid group undergo hydrogen transfer from the carboxylic acid group to the α -substituent. This mechanism occurs for conformer III of lactic acid and conformer II of glycine and valine.

Thus, conformation specific reactivity of radical cation intermediates is solely directed by two specific properties of the molecular ion: 1. specific localization of the charge; and 2. initial intramolecular hydrogen bonding structure. The hydrogen bonding structure of these species can favor or hinder charge migration and hydrogen transfer. This conclusion is consistent with the idea of a ‘charge directed reactivity’ of peptides observed by Weinkauff, *et al.*^{27(a)} Their study finds that fragmentation products of peptides, generated by vertical ionization, depend upon specific peptide sequence that can assist or hinder hole migration. Weinkauff, *et al.*^{27(b)} later modeled charge propagation within a peptide as arising from a steric requirement for bond alignment along the peptide chain to facilitate hole migration. We also find similar steric requirements for charge transfer to occur from the SOMO on the α -substituent to the C_{α} - $C_{\text{carboxylic}}$ bond for α -substituted carboxylic acids. Thus a ‘through bond’ mechanism⁴⁸ is supported for charge migration. Knowledge of the relative timescales of

charge transfer, hydrogen transfer, and structural change is essential in order to obtain further detailed insights on the interplay of these three processes for the reactivity of radical cation intermediates of α -substituted bioactive carboxylic acids.

Radical cationic pyruvic acid shows a special stability with respect to lactic acid, glycine, and valine. A qualitative comparison of TOMFS intensities between the parent ion and fragment ion signals for pyruvic acid indicates that less than 45% of the parent ion of pyruvic acid dissociates following VUV ionization at 10.5 eV. The extra stability of pyruvic acid radical cation has recently been proposed and related to π -delocalization of the positive charge following enolization of the α -keto form.¹² The enol form of pyruvic acid on the cationic surface is predicted to be exothermically stabilized by more than 20 kcal/mol (CASSCF(9,8)/6-31G(d) result). A similar stabilizing factor is absent for the radical cation intermediates of glycine, valine, or lactic acid.

To study the role of the local ion environment on conformation specific reactivity and stability of isolated biomolecules further, we have started experiments on simple α -substituted amides, β -hydroxy/thiol amino acids. All these hitherto unexplored systems are in principle open to IR-VUV photoionization spectroscopic study. Other experiments that would be helpful in further testing conformation specificity for the reactivity of radical cation intermediates include velocity map imaging experiments to measure different components of translational energy distribution following C_{α} - $C_{\text{carboxylic}}$ bond dissociation from different conformers, and photoelectron spectroscopy to determine the molecular ion states produced through ionization. Moreover, theoretical exploration of the relative time scales of charge transfer, hydrogen transfer,

and structural rearrangement for a particular conformer of bioactive carboxylic acids would be advantageous.

10.7 Conclusions

In this chapter, the conformation specific and charge directed reactivity of the radical cation intermediates of lactic acid, pyruvic acid, glycine, and valine is illustrated. The conformation specificity and charge directed reactivity suggested for these systems can be generalized for radical cation intermediate behavior for all bioactive carboxylic acids. Lactic acid, glycine, and valine, when ionized to the lowest vertical ionization region, undergo complete and conformation specific decomposition reactions. Conformation specific fragmentation patterns of these nascent radical cationic intermediates are clearly demonstrated by recording different IR spectra (corresponding to different conformations) monitoring different fragment TOFMS signals.

Ab initio calculations show that the electronic hole (positive charge) in the nascent radical cationic lactic acid, glycine, and valine is primarily localized on the hydroxyl O or amine N atom if the α -substituent donates a hydrogen bond to the carboxylic acid group (conformers I and II of lactic acid, and I and II of glycine and valine). This structure favors either C_{α} - $C_{\text{carboxylic}}$ bond dissociation or hydrogen transfer from the α -substituent to the carboxylic acid group. The actual mechanism, however, depends on the relative orientation of the SOMO with respect to the C_{α} - $C_{\text{carboxylic}}$ σ -bond and the activation barrier associated with the reaction coordinate. If the α -substituent accepts a hydrogen bond from the carboxylic acid OH group (conformer III of lactic acid and II of glycine and valine), a stabilization effect due to hydrogen

bonding lowers the energy of the lone pair orbitals of the α -substituent. In this case, the hole is localized on the carboxylic acid group, and this structure facilitates hydrogen transfer from carboxylic acid OH to the α -substituent. Thus, different structural orientations of the molecule give rise to different fragmentation patterns in α -hydroxy and α -amino aliphatic bioactive carboxylic acids: the reactivity of these systems is primarily governed by the local charge distribution.

The pyruvic acid radical cation, generated near its lowest vertical ionization region, does not completely undergo fragmentation. Two different conformers (I and II) of pyruvic acid are identified by recording IR spectra monitoring the parent ion signal. Both conformers undergo, to some extent, the C $_{\alpha}$ -C_{carboxylic} bond dissociation; however, theoretical calculations infer that different exothermicities of the reaction associated with the two conformers may provide different energy distributions for the products (COOH and H₃CCO⁺).

The present findings suggest that the reactivity of radical cations of bioactive carboxylic acids is dependent upon their initial conformations, and thus on their anisotropic environments. Under conditions of the early earth (more exposure to VUV radiation), the special stability of pyruvic acid against photochemical damage could possibly provide a preservative basis for the energy derived from metabolic process.

10.8 Acknowledgment

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Supplementary Information

Table 10.T1: Computed vertical ionization energies (VIEs) at the MP2/aug-cc-pVDZ and CASSCF(9,8)/6-31G(d) levels of theory. A comparison with experimental values is also given. Experimental results are based on photoelectron spectroscopy.¹

Compound	Conformation	Calc. VIE (eV) MP2/aug-cc-pVDZ	Calc. ion states CAS(9,8)/6-31G(d)		Expt. VIE (eV)	
			State	Excitation energy (eV)	D ₀	D ₁
Lactic Acid	I	11.00	D ₀ , np _O	0.0	-	-
			D ₁ , nσ _O	1.7		
	II	10.44	D ₀ , nσ _O	0.0		
			D ₁ , nπ _O	1.2		
	III	10.90	D ₀ , nσ _O	0.0		
			D ₁ , nπ _O	1.0		
Pyruvic Acid	I	10.49	D ₀ , nσ _O	0.0	10.42	12.31
			D ₁ , nσ _O	2.0		
	II	10.92	D ₀ , nσ _O	0.0		
			D ₁ , nπ _O	3.2		
	III	11.00	D ₀ , nσ _O	0.0		
			D ₁ , nπ _O	0.0		
Glycine	I	10.22	D ₀ , nσ _N	0.0	10.00	11.11
			D ₁ , π _{COOH}	4.3		
	II	10.28	D ₀ , nσ _O	0.0		
			D ₁ , π _{COOH}	1.2		
	III	10.12	D ₀ , np _N	0.0		
			D ₁ , nσ _O	4.0		

Knowledge of specific molecular ion state is important for subsequent study of dissociation mechanism and dynamics of a cation. A comparison between the computed VIE and the experimental ionization energy (10.5 eV) has, therefore, been performed to assess which molecular ion state is relevant to the experimental observations. Theoretical estimates of VIE could be performed using an outer-valance Green's function method; however, here we determine lowest VIE by explicitly calculating the energy difference between neutral and cation at the FC geometry (ground state

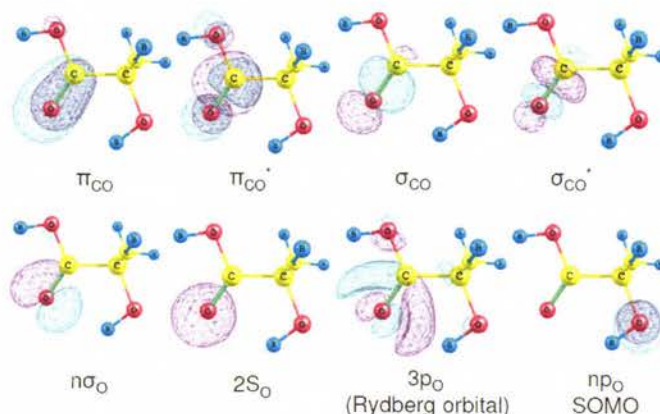
minimum). The VIE for lactic acid, pyruvic acid, glycine calculated at their MP2/aug-cc-pVDZ optimized FC geometry are listed in Table 10.T1. MP2/aug-cc-pVDZ calculation shows that lowest VIE of pyruvic acid and glycine are 10.4 and 10.0 eV, respectively, which are in good agreement with the experimental values obtained from molecular photoelectron spectroscopy.¹ This comparison reveals that the MP2/aug-cc-pVDZ level of theory calculates reasonably accurate lowest VIE. To the best of our knowledge, to date, ionization energy for lactic acid is not experimentally determined. A comparison of ionization energy (10.5 eV) used in the experimental work with the calculated VIEs, however, undoubtedly indicates that all these molecules are excited to their D_0 ground ion state.

References:

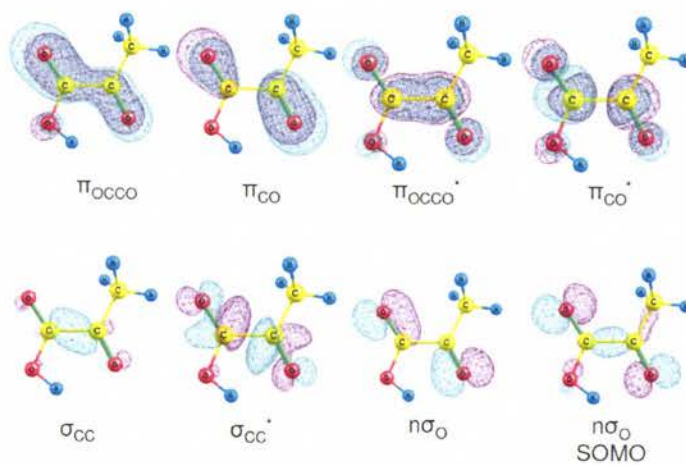
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Figure 10.S1: Natural orbitals used in the active space for CASSCF calculations for radical cationic lactic acid, pyruvic acid, glycine. These orbitals comprise the active space with 9 electrons in 8 orbitals. Only orbitals of the lowest energy conformer of lactic acid, pyruvic acid, and glycine are shown below.

Lactic Acid



Pyruvic Acid:



Glycine:

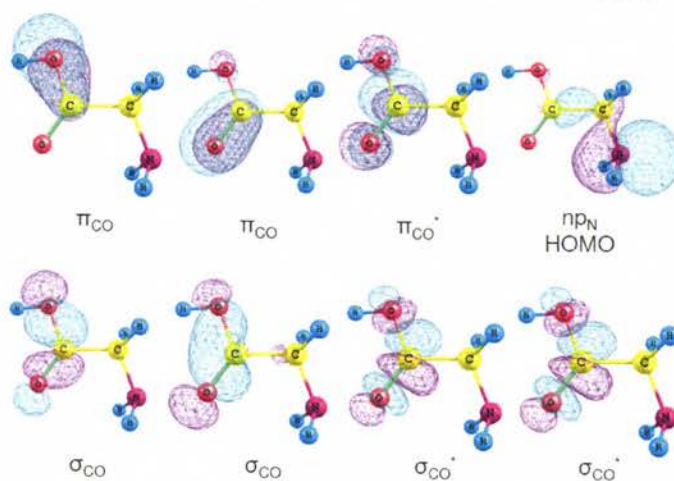
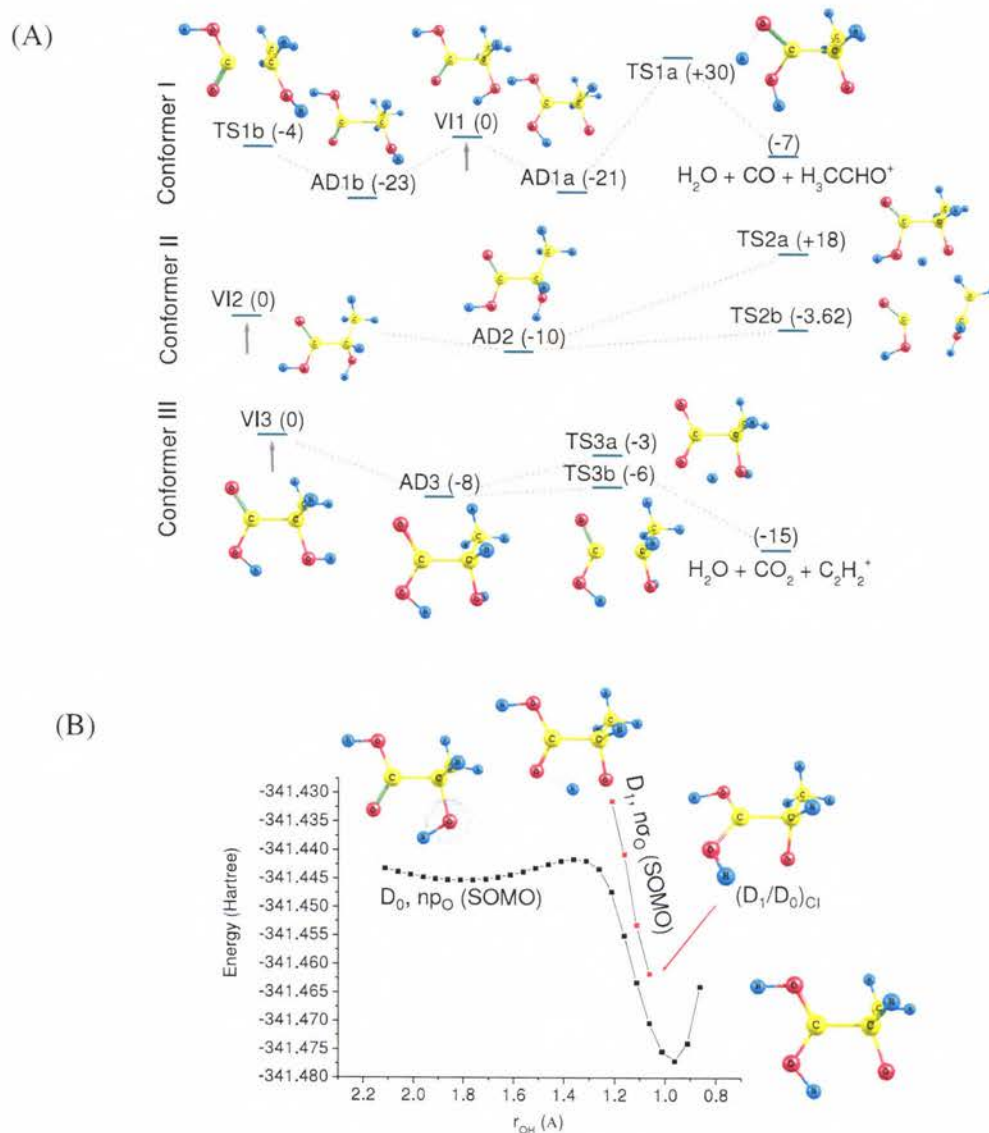


Figure 10.S2: (A) The potential energy diagram along the two reaction pathways (hydrogen transfer (denoted with a suffix 'a') and COOH elimination (denoted with a suffix 'b') for different conformers of radical cationic lactic acid in the ground doublet electronic state obtained at MP2/aug-cc-pVDZ level of theory. Vertical arrows show the FC points. (B) Hydrogen transfer pathways for conformer I with location of the $(D_1/D_0)_{CI}$ conical intersection computed at CASSCF(9,8)/6-31G(d) level of theory.



Decomposition pathways for lactic acid radical cation computed at the MP2/aug-cc-pVDZ level are shown in Figure 10.S2(A). Two adiabatic geometries are optimized for the conformer I: one in the hydrogen transfer (from α -substituent to

COOH group, denoted with a suffix 'a') and another in C_{α} - $C_{\text{carboxylic}}$ bond dissociation (denoted with a suffix 'b') reaction coordinates. No activation barrier is predicted for the initial step in the hydrogen transfer process. Subsequent H_3CCHO^+ product formation reaction possesses an activation barrier of 51 kcal/mol with respect to the adiabatic point. Direct C_{α} - $C_{\text{carboxylic}}$ bond dissociation, however, has an activation barrier of 19 kcal/mol with respect the adiabatic point. Therefore, MP2/aug-cc-pVDZ level of theory predicts C_{α} - $C_{\text{carboxylic}}$ bond dissociation as the minimum energy pathway for the conformer I of lactic acid.

Only one adiabatic ion geometry, on the other hand, is optimized for both conformer II and III. An activation barrier of 28 kcal/mol is calculated for hydrogen transfer from the α -hydroxy to COOH, whereas C_{α} - $C_{\text{carboxylic}}$ bond dissociation possesses an activation barrier of 6 kcal/mol for conformer II. Thus, calculation predicts C_{α} - $C_{\text{carboxylic}}$ bond dissociation to be minimum energy pathway for both conformer II and III. C_{α} - $C_{\text{carboxylic}}$ is also predicted to be the minimum energy pathway for conformer III.

In contrast, the CASSCF level of theory predicts a different scenario for conformer I. The potential energy diagram computed at CASSCF level of theory is depicted in Figure 9 in the paper. CASSCF level of theory predicts an activation barrier of 0.9 kcal/mol for the initial hydrogen transfer from the α -substituent to the COOH for conformer I. The activation barrier for subsequent H_3CCHO^+ product formation is calculated to be of 9 kcal/mol, which is well below the available energy stored in the vibrational degrees of freedom of the molecule due to vertical to adiabatic evolution. C_{α} - $C_{\text{carboxylic}}$ dissociation energy is predicted to have much higher activation energy

(~11 kcal/mol). Thus, the hydrogen transfer pathway is calculated to be minimum energy pathway for conformer I at the CASSCF level of theory, whereas MP2 results predict C $_{\alpha}$ -C_{carboxylic} bond dissociation as minimum energy pathway. This discrepancy between MP2 and CASSCF results is found to persist at the CASPT2//CASSCF level of theory.

At the CASSCF level, one (D₁/D₀)_{CI} conical intersection is localized in the hydrogen transfer reaction coordinate, as illustrated in Figure 10.S2(B). Adiabatic energy gap between D₁ and D₀ surface in the conical intersection is calculated to be 400 cm⁻¹, indicating a strong nonadiabatic coupling between D₁ and D₀ surfaces. In many organic molecules (containing C, H, N, O) ground electronic surface topology is found to be affected by the proximity of the upper excited electronic surface near the conical intersection.¹ Depending on the strength of the nonadiabatic coupling in the region of conical intersection, the ground state surface is repelled to lower energy. Such a surface topological change is assessed only by multiconfigurational methods such as CASSCF, CASPT2, MRCI. Mono-configurational methods, such as HF, MP2, often overestimate the energy barrier of a transition state near the conical intersection because they do not model how the ground surface topology can be altered by the proximity of the upper excited electronic state surface near the conical intersection due to nonadiabatic coupling. Therefore, multiconfigurational methods are expected to provide a more reasonable theoretical picture of the ion states which are usually very close in energy.

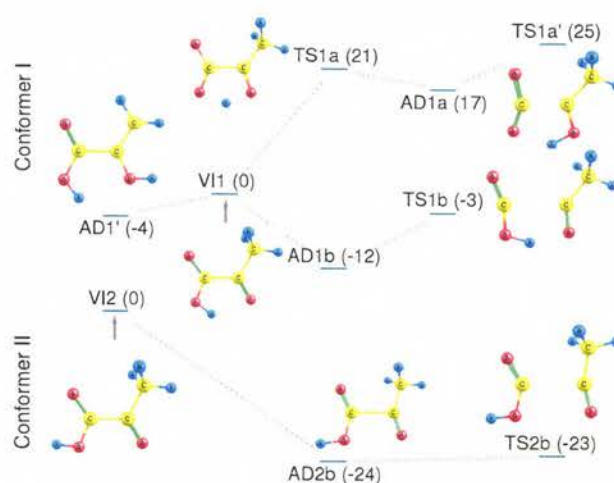
Thus, hydrogen transfer is considered to be the minimum energy pathway for conformer I of lactic acid. Although major discrepancies are found between results

obtained at the MP2 and CASSCF levels of theory for the conformer I, both levels of theory provide mutually consistent results for conformer II and III.

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Figure 10.S3: Potential energy diagram of different conformers of radical cationic pyruvic acid in the ground doublet ion state obtained at the MP2/aug-cc-pVDZ level of theory.



Pyruvic acid is a unique molecule among the α -substituted bioactive carboxylic acids discussed here because it displays keto-enol tautomerism. This molecule changes the tautomeric preferences when going from the neutral to ionized form.¹

The keto form of neutral pyruvic acid is more stable (by 7 kcal/mol) than the enol form; however, the enol form is favored over the keto form for ionized pyruvic acid. At the MP2/aug-cc-pVDZ level we find that keto-enol tautomerism is exothermic by 4 kcal/mol for conformer I, 30 kcal/mol for conformer II, and 20 kcal/mol for conformer III. The CASSCF results are close to the MP2 results for conformer II and III, but the CASSCF level of theory predicts a 12 kcal/mol exothermicity associated

with keto-enol tautomerism for the conformer I. The unusual stability of the enol form for the radical cationic pyruvic acid comes from the π -delocalization of the charge and additional hydrogen bonds between α -substituent and the carboxylic acid group or vice versa.¹

The potential energy diagram for pyruvic acid radical cation computed at the MP2/aug-cc-pVDZ level of theory is given in Figure S3. The keto form of radical cationic pyruvic acid dissociates to COOH and H₃CCO⁺ with no activation barrier for the three conformers. MP2/aug-cc-pVDZ theory predicts an exothermicity of 3 kcal/mol for conformer I, 23 kcal/mol for conformer II, and 28 kcal/mol for conformer III associated with C _{α} -C_{carboxylic} bond dissociation. CASSCF on the other hand finds that exothermicities associated with C _{α} -C_{carboxylic} bond dissociation are 23 kcal/mol for conformer I, 7 kcal/mol for conformer II, and 8 kcal/mol for conformer III. Thus both levels of theory indicate that C _{α} -C_{carboxylic} is the minimum energy decomposition pathway for the keto form of the radical cationic pyruvic acid.

Only conformer I can potentially undergo hydrogen transfer from the carboxylic acid group to the α -keto substituent. Computation at the MP2/aug-cc-pVDZ and the CASSCF/6-31G(d) levels reveals an activation barrier of 21 and 8 kcal/mol, respectively from the FC point, indicating that hydrogen transfer from COOH to the α -substituent is an endothermic process and therefore, is unlikely to happen.

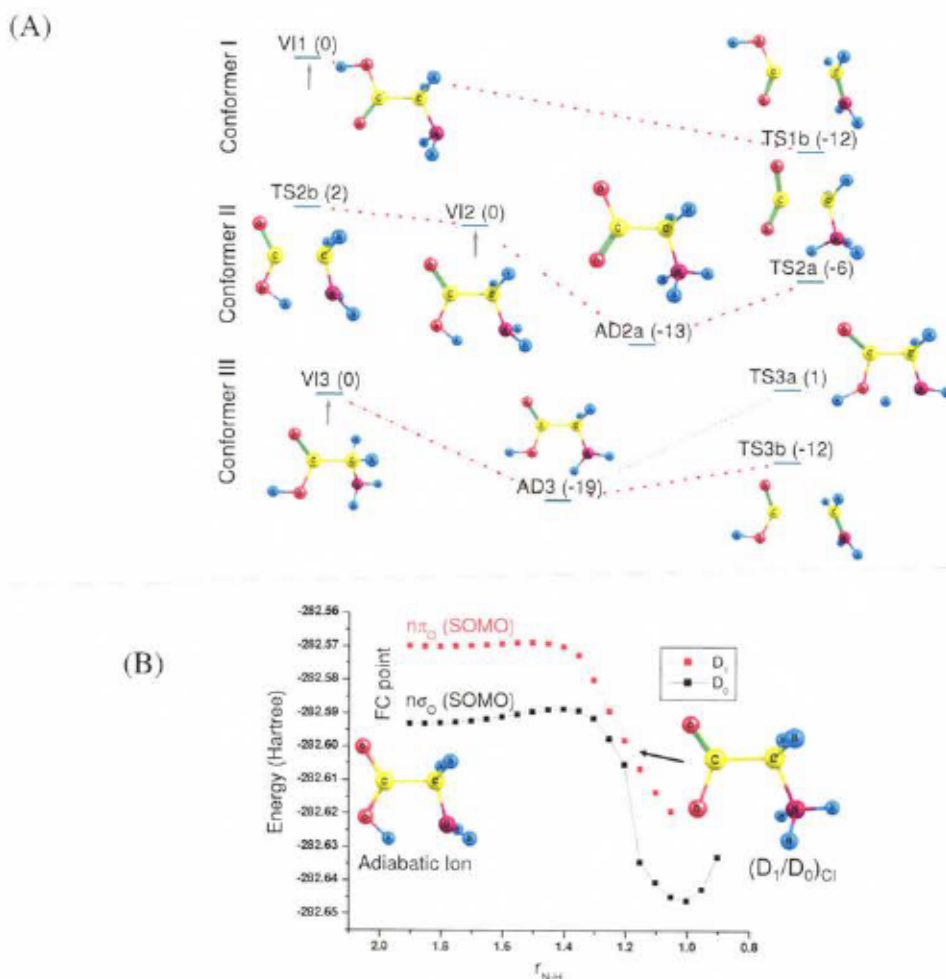
Electronically excited ion states for pyruvic acid do not exist in close proximity to the ground doublet ion state. CASSCF predicts excitation energy of 2 eV for conformer I, 3.2 eV for conformer II, and 3.1 eV for conformer III. The D₁ state for the conformer II and III corresponds to removal of an electron from the π system of the

neutral; however, that of conformer I is associated with removal of an electron from nonbonding $n\sigma_O$. Because of this large energy difference, nonadiabatic coupling is not an important factor contributing to the ground ion state surface of pyruvic acid. Consequently, MP2 and CASSCF provide mutually consistent results.

References:

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Figure 10.S4: (A) Different decomposition pathways of glycine radical cations computed at MP2/aug-cc-pVDZ. (B) Hydrogen transfer pathway for conformer II of glycine with localization of $(D_1/D_0)_{CI}$.



D_0 potential energy diagram for different conformers and structures of different critical points computed at MP2/aug-cc-pVDZ level of theory, for the glycine radical cation are depicted in Figure 10.S4(A). Vertical arrows in the figures indicate the FC points on the D_0 surface. Transition state energy associated with C_α - $C_{\text{carboxylic}}$ bond dissociation for conformer I is predicted to be lower (by 12 kcal/mol at MP2 and 17 kcal/mol at CASSCF) in energy than that of the FC geometry on the D_0 surface. IRC calculation reveals that the corresponding reaction pathway from the FC point to the C_α - $C_{\text{carboxylic}}$ bond dissociation pathway is barrierless. An adiabatic geometry, on the other hand, is optimized for conformer I (not shown in the figure) in the hydrogen transfer (from α -NH₂ group to the COOH group) reaction coordinate. Both MP2 and CASSCF levels of theory predict planar geometry for the H₂N-COOH moiety of conformer I of the glycine ion. An activation barrier of 17 kcal/mol at the CASSCF level and 12 kcal/mol at the MP2 level is predicted for the subsequent hydrogen transfer reaction from α -NH₂ group to the COOH group. Therefore, C_α - $C_{\text{carboxylic}}$ bond dissociation pathway is predicted to be the minimum energy pathway (associated with lowest activation barrier) for conformer I.

At CASSCF level of theory (see Figure 10.11 of text), one adiabatic geometry is optimized for conformer II, which is common in both C_α - $C_{\text{carboxylic}}$ bond dissociation and hydrogen transfer pathways. The adiabatic geometry is stabilized by 9 kcal/mol (CASSCF) caused by vertical to adiabatic evolution of the ion. Following this adiabatic point on the D_0 surface, two reaction pathways are identified: one associated with C_α - $C_{\text{carboxylic}}$ bond dissociation with an activation barrier of 2 kcal/mol and another related to hydrogen transfer pathway from COOH to the α -NH₂ group with an activation

barrier of 0.8 kcal/mol. Following hydrogen transfer reaction, another adiabatic geometry is optimized which is further stabilized by 18.8 kcal/mol at CASSCF level of theory. Subsequent CO₂ elimination pathway is predicted to have an activation barrier of 25 kcal/mol which is lower (by 2 kcal/mol) than the calculated available excess energy ($VIP-ADI+\Delta H_{\text{reaction}}$) stored in the vibrational degrees of freedom.

MP2 results, on the contrary, provide a different scenario for glycine conformer II on D₀. MP2 theory predicts an endothermic activation barrier of 2 kcal/mol associated with C_α-C_{carboxylic} bond dissociation from the FC point on the D₀ surface (see Figure S4(A)); however, the hydrogen transfer pathway is calculated to have zero activation barrier and the adiabatic geometry in this reaction coordinate following hydrogen transfer is stabilized by 13 kcal/mol. The subsequent CO₂ elimination pathway needs to circumvent a barrier of 7 kcal/mol, which is much lower than the CASSCF value (25 kcal/mol). This discrepancy between MP2 and CASSCF results may be caused by near degeneracy effects, which can only be assessed by multiconfigurational methods. Thus CASSCF results are to be considered much more realistic than are the MP2 results.

To obtain further information on the ground doublet ion surface topology we investigate the influence of (D₁/D₀)_{CI} conical intersection on the ground surface. CASSCF calculation reveals that the upper D₁ electronic surface for the conformer II is highly nonadiabatically coupled with D₀ surface along the hydrogen transfer reaction coordinate. A (D₁/D₀)_{CI} conical intersection is localized in the hydrogen transfer reaction coordinate of conformer II, which is illustrated in Figure 10.S4(B). The adiabatic energy difference between the D₀ and D₁ surfaces near the (D₁/D₀)_{CI} conical

intersection is computed to be 500 cm^{-1} , which suggests strong nonadiabatic coupling between the D_1 and D_0 surfaces.

Therefore, the major discrepancy found between MP2 and CASSCF results arises from the alteration of the surface topologies caused by presence of conical intersections. In spite of existing topological anomalies, both levels of theory predict that hydrogen transfer is the minimum energy pathway for conformer II.

C_α - $C_{\text{carboxylic}}$ bond dissociation is predicted to be the minimum energy pathway for conformer III at both CASSCF and MP2 levels of theory. One adiabatic point exists on the D_0 surface for conformer III, which shows a planar H_2N -COOH moiety similar to that of conformer I. The adiabatic geometry is stabilized by 19 kcal/mol at the MP2 level (22 kcal/mol at CASSCF). Following the adiabatic point on the D_0 surface, a C_α - $C_{\text{carboxylic}}$ bond dissociation pathway is identified to have an activation barrier of 7 kcal/mol at MP2 (16 kcal/mol at CASSCF). The hydrogen transfer pathway possesses a much higher activation barrier (20 kcal/mol at MP2 and 27 kcal/mol at CASSCF).

Therefore, theoretical calculation shows that C_α - $C_{\text{carboxylic}}$ bond dissociation pathway is the minimum energy pathway for conformers I and III of glycine. The C_α - $C_{\text{carboxylic}}$ bond dissociation pathway possesses different exothermicities for these two conformers. The hydrogen transfer pathway is the minimum energy pathway for conformer II.

Following ionization, the hole density is mostly localized on the O end of carbonyl group of glycine conformer II, which increases the acidity of the carboxylic acid group. Consequently, this conformer favors hydrogen transfer from COOH to the NH_2 group for the initial step of the decomposition. The hole density is localized at the

N of the amine group for conformers I and III of glycine. Therefore, subsequent reactivity of the nascent radical cation of glycine conformers I and III is expected to be different from that of conformer II. The SOMO (np_N) is parallel to the C_α - $C_{\text{carboxylic}}$ bond for conformer I. This orbital alignment favors charge transfer from N to the C_α - $C_{\text{carboxylic}}$ bond, rendering C_α - $C_{\text{carboxylic}}$ bond dissociation a barrierless process for conformer I; however, the SOMO (np_N) is perpendicular to the C_α - $C_{\text{carboxylic}}$ bond for conformer III. Thus charge transfer from the N to C-C bond requires rotation of C-N bond in order to align the np_N parallel to the C_α - $C_{\text{carboxylic}}$ bond for conformer III. This process requires an activation barrier.

CHAPTER 11

Unfinished Work and Future Directions: Intrinsic Folding of Peptides

Controls the Reactivity of Their Radical Cation Intermediates

11.1 Introduction

Protein folding, which allows the peptide chain to fold into its characteristic and functional three dimensional structure, plays an important role in protein chemistry.¹⁻⁸ The folds (or turns) in protein are characterized by a hydrogen bond bridging the hydrogen bond acceptor CO and hydrogen bond donor NH sites of different residues along the backbone in polypeptide chains. For instance, β -turns in protein are based on C_{10} interaction, named after the ten membered ring formed due to intramolecular hydrogen bonding interaction between CO and NH groups, as illustrated in Figure 11.1. The β -turn is the smallest secondary structure of proteins: it is often found to be in competition with other turns, such as γ -turns, β -strands (based on C_7 and C_5 interactions, respectively, see Figure 11.1), and helices (based on more remote interaction such as C_{13} , not shown in Figure 11.1).

C- and N-termini protected amino acids can be referred to as model peptide analogues as they enable investigation of the intrinsic conformational preferences of the backbone on each residue. Although a number of conformations of these small model peptides are possible according to Ramachandran terminology¹ based on the ϕ and ψ

dihedral angles, γ -turns and β -strands show hydrogen bonded structures. γ -turns and β -strands differ from each other by their intrinsic hydrogen bonding architectures.

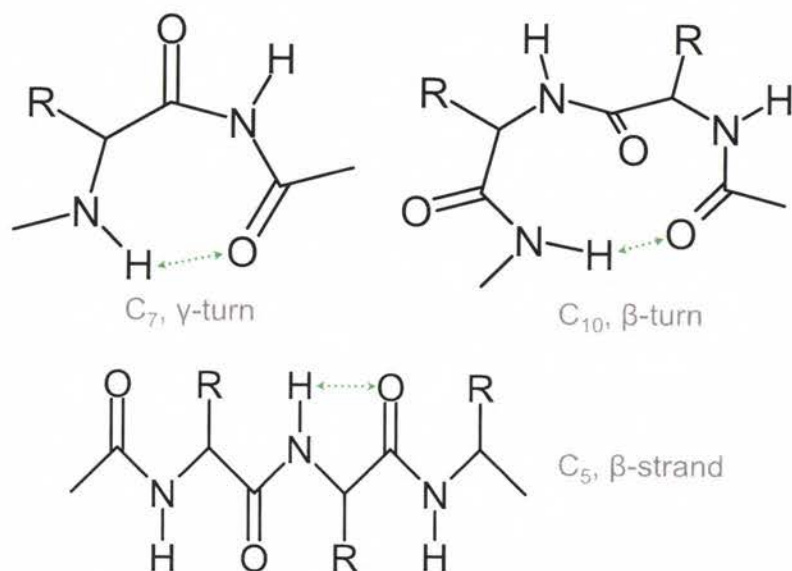


Figure 11.1: Generic folding within a peptide sequence. Different intramolecular hydrogen bonds are shown with their generic names.

Several studies performed recently have found that hydrogen bonding plays an important role in determining reactivity of radical cations of peptides containing basic residues.⁹⁻¹⁶ Understanding the reactivity of these peptide radical cations is of great importance.¹⁷ The fragmentation pathways of peptide radical cations can be altered based on location of the charge. In the previous chapter we have seen that the localization of positive charge and subsequent reactivity of radical cationic amino acids, hydroxy acids, and keto acids are conformation specific. In other words, different hydrogen bonding architectures change the local electronic environment, which in turn, change the reactivity of these species. One can ask a similar question for small

peptides: can different foldings, which arise due to different types of hydrogen bonding interactions, control the radical cationic reactivity of peptides?

For this study a number of peptide analogues such as $\text{CH}_3\text{CO-Gly-NH}_2$, $\text{CH}_3\text{CO-Gly-Gly-NH}_2$ and a dipeptide Gly-Gly can be selected. $\text{CH}_3\text{CO-Gly-NH}_2$ can form both γ -turn and β -stand, however, it cannot form β -turn. $\text{CH}_3\text{CO-Gly-Gly-NH}_2$ can, on the other hand, form β -turn, β -stand, and γ -turn. A future direction of the research presented in the Part 2 of this thesis is to reach a general conclusion on how these types of foldings control the radical cationic reactivity of peptides. Radical cation intermediates of peptide analogues can be generated through single photon VUV (10.5 eV) ionization and their folding specific reactions can be monitored using IR-VUV spectroscopy.

11.2 Preliminary Results on $\text{CH}_3\text{CO-Gly-NH}_2$

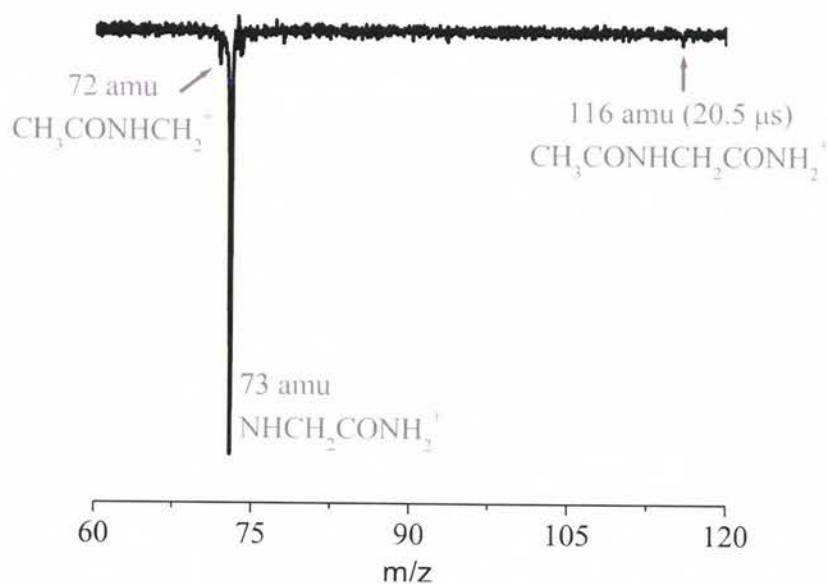


Figure 11.2: TOFMS of $\text{CH}_3\text{CO-Gly-NH}_2$ at 118 nm. The gas phase sample of this model peptide is obtained by laser ablation, as described in Appendix I of this thesis.

Figure 11.2 shows TOFMS of $\text{CH}_3\text{CO-Gly-NH}_2$ peptide analogue obtained at 118 nm photoionization. Three important mass signals correspond to $m/z=73$, 72, and 116 amu. Mass signal at 116 amu is attributed to the parent ion. 100 mV signal intensity is obtained at 73 amu fragment mass channel. The fragment signal at 73 amu can be generated through different mechanisms. CASSCF calculation, however, shows that vertical to adiabatic evolution of the C_7 conformer (most stable conformer of $\text{CH}_3\text{CO-Gly-NH}_2$, see Figure 11.3) leads to hydrogen transfer from NH_2 to CO, and subsequent HNCO elimination can generate the fragment signal at 73 amu. Experimental conform, however, requires IR-VUV study.

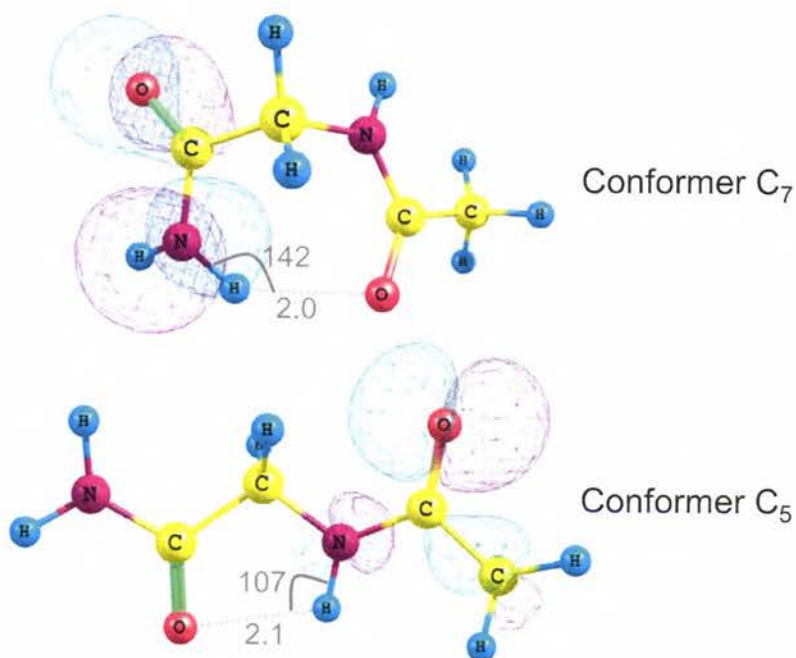


Figure 11.3: Two important conformers of $\text{CH}_3\text{CO-Gly-NH}_2$ indicating their S_0 stable structures (MP2) with D_0 SOMO densities (CASSCF). C_7 is the most stable conformer.

Figure 11.3 shows MP2 (S_0) optimized structures of C_7 and C_5 conformers of the $\text{CH}_3\text{CO-Gly-NH}_2$ peptide analogue with the CASSCF calculated D_0 SOMO

densities superimposed. For most stable conformer C_7 , the SOMO is primarily localized on NH_2CO end of the molecule and for conformer C_5 , the SOMO is primarily localized on CH_3CO end of the molecule. Therefore, the localization of charge in the $\text{CH}_3\text{CO-Gly-NH}_2$ peptide analogue is folding specific.

The SOMO of conformer C_7 arises from removal of an electron from the lone pair orbital of the NH_2 moiety; and the SOMO of conformer C_5 arises from removal of an electron from the carbonyl O lone pair orbital. Localization of charge on the NH_2CO moiety of C_7 conformer increases the acidity of NH_2 group, which facilitates hydrogen transfer along the hydrogen bonded network in C_7 conformer. Computation at CASSCF(9,8)/6-31G(d) level of theory predicts no activation barrier for this hydrogen transfer process and the $(\text{CH}_3)\text{C}(\text{OH})\text{N}(\text{H})\text{CH}_2^+$ fragment is predicted to be generated mostly from conformer C_7 of $\text{CH}_3\text{CO-Gly-NH}_2$. Further IR-VUV experiments and calculations at the CASSCF level are necessary to unveil the folding specificity in the reactivity of different peptides in gas phase.

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APPENDIX I

Experimental Techniques

Introduction

The experimental setup utilized for the work discussed in this thesis consists of ns and fs laser systems, a supersonic jet expansion pulsed nozzle (Jordon and General valve), and two vacuum chambers: a time of flight mass spectrometer (TOFMS) chamber and an LIF (laser induced fluorescence) chamber. This chapter illustrates and discusses in detail the experimental techniques used in the exploration of excited electronic state decomposition of energetic materials and ion state decomposition of bioactive carboxylic acids.

1. Generation of Gas Phase Molecules

Experiments presented in this thesis require intact neutral gas phase sample molecules. To obtain a supersonic molecular beam of non-volatile, thermally unstable solid samples like RDX, a laser desorption (LD) technique is adopted and combined with the supersonic jet technique. This is accomplished using a desorption nozzle assembly similar to that described previously by Smalley.¹ In this assembly a LD extension block is attached to a pulsed supersonic nozzle (Jordan Company, PSV). The extension block consists of a stepper motor and gears, a shaft for a sample holder, a sample holder, a flow channel, a laser beam inlet hole, and a laser beam alignment hole,

as illustrated in Figure 1. At the center of the extension block, a flow channel of 2 mm diameter and about 6 cm long is aligned with the nozzle orifice (2 mm diameter).

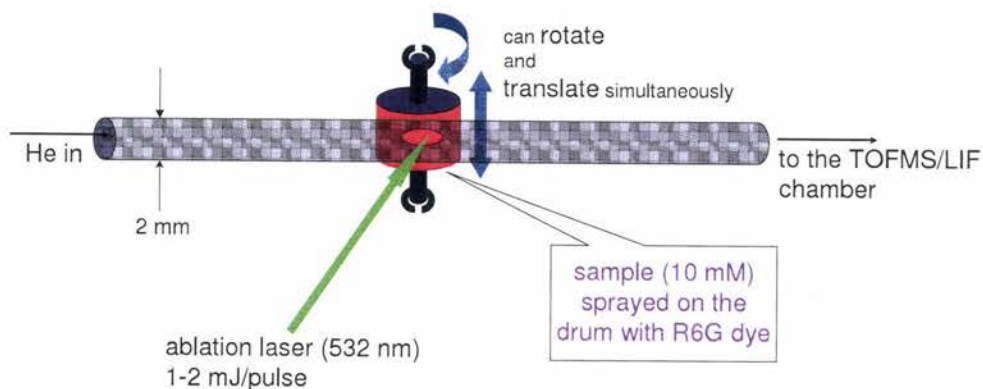


Figure 1: Interior design of a LD extension block is attached to a pulsed supersonic nozzle (Jordan Company, PSV).

The ablation laser beam inlet channel of 1 mm diameter is perpendicular to the gas/sample flow channel. The sample holder is made of Al and has a right circular cylindrical shape. The dimensions of the Al drum are 38.79 mm and 27.03 mm for the outer diameter and the inner diameters, respectively, with a 20 mm height. The sample drum is installed in the extension block on a shaft that can be simultaneously rotated and translated through the combination of a stepper motor and gears. The whole sample setup is designed for the sample surface to be tangential to the gas flow channel.

The use of laser desorption as a source of molecules produces a stable supply of sample vapor pulses for extended periods of time. This condition can be achieved by preparing a porous and smooth surface for even deposition of a sample. In the experiments presented in this thesis, such a surface is obtained using an aluminum oxide thin film coated on an aluminum drum. The aluminum oxide thin film is generated by plasma electrolytic oxidation.² An Al drum as anode is immersed into the

electrolytic solution, and dc voltage of 120-150 V is applied to maintain a current of 1.0-1.5 A. The electrolytic solution is composed of NaF, $\text{Na}_2\text{B}_4\text{O}_7$, $(\text{NH}_4)_2\text{HPO}_4$, and NaH_2PO_4 with the concentration of 0.6, 0.1, 0.1, and 0.5 M, respectively.³ Under these conditions, a plasma is formed on the surface of the Al drum and oxidizes it. A $\gamma\text{-Al}_2\text{O}_3$ film about 10 μm thick can be produced on the Al drum surface within 10 min. Instead of Al_2O_3 coated Al drum, a piece of porous filter paper attached to an Al metal drum can also be used as a porous and smooth surface for even deposition of a sample.

Equimolar quantities (4×10^{-5} mol) of the sample and a matrix substance are dissolved in an appropriate solvent, mainly acetone in the experiment. The laser dye R6G is chosen as a matrix substance because of its absorption coefficient at 532 nm. A mixture of the sample and R6G at 1:1 molar concentration is sprayed on the prepared drum. An air atomizing spray nozzle (Spraying System Co.) with siphon pressure of 20 psig is used to deposit the sample/R6G on the drum surface. During the spraying, the drum is heated with halogen lamp to help solvent dry and rotated with clock motor for homogeneous coating.

2. Time-Of-Flight Mass Spectrometry

A population of ions moving in the same direction and having a distribution of masses but a constant kinetic energy, will have a corresponding distribution of velocities. Thus if the ions travel a fixed distance, they will be separated in time according to their mass to charge ratio. This concept is the working principle of time-of-flight mass spectrometry. A generic picture of TOFMS working principle is illustrated in Figure 2, which shows initial generation of molecular beam, collection of internally cold molecules through a skimmer, fragmentation/ionization of the molecules,

and subsequent acceleration of the ions followed by detection by microchannel plate detector (MCP).

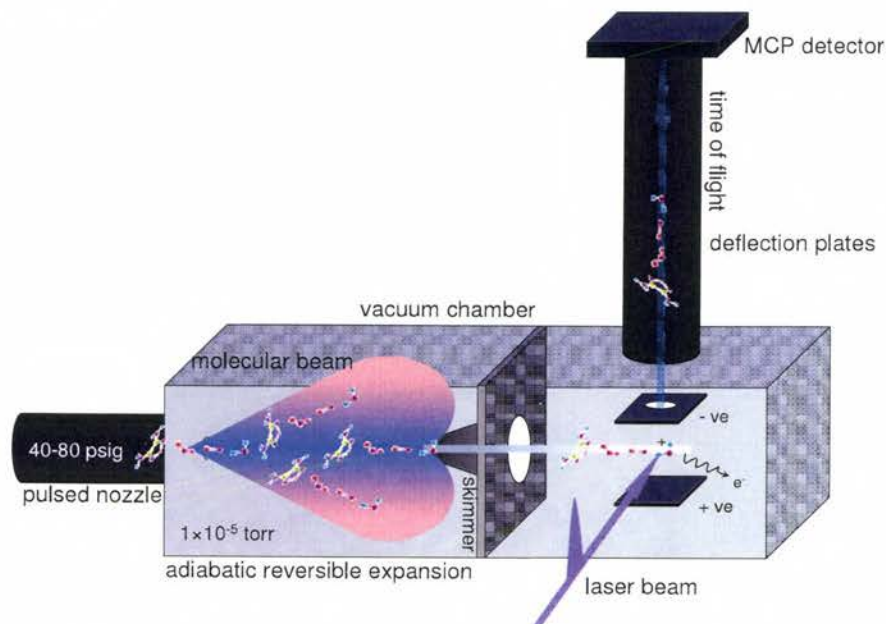


Figure 2: A generic picture of TOFMS, which shows generation of molecular beam, collection of cold molecules through skimmer, fragmentation/ionization of the molecules by laser, acceleration of the ions to the MCP detector through flight tube.

For our experiment, the gas phase neutral parent molecules are seeded into molecular beam, they fragment following electronic excitation, and their products are ionized in the ionization region of the TOFMS using REMPI. The positive ion produced in the ionization region is accelerated by +4000 V volts towards a microchannel plate (MCP) detector through a field free flight tube. Unknown mass of the ion can be determined from the flight time. TOF mass calibration is performed using the flight times of at least two known masses with the following equation:

$$\frac{m}{z} = at^2 + b \quad (1)$$

For our system equation (1) gives $t = -1.3875 + 1.897\sqrt{m}$ where the time is in microsecond.

3. Laser Induced Fluorescence

A molecule must be ionized in order to detect it in TOFMS. Sometimes, ionizing a molecule might be a daunting task because of several reasons such as unavailability of correct laser wavelength and high ionization potential of a molecule. Under these conditions, a molecule can be detected from its characteristics fluorescence. In laser induced fluorescence (LIF) an electronic transition of a molecule is driven using a tunable nanosecond laser and any fluorescence generated is monitored. The general experimental scheme is illustrated in Figure 3.

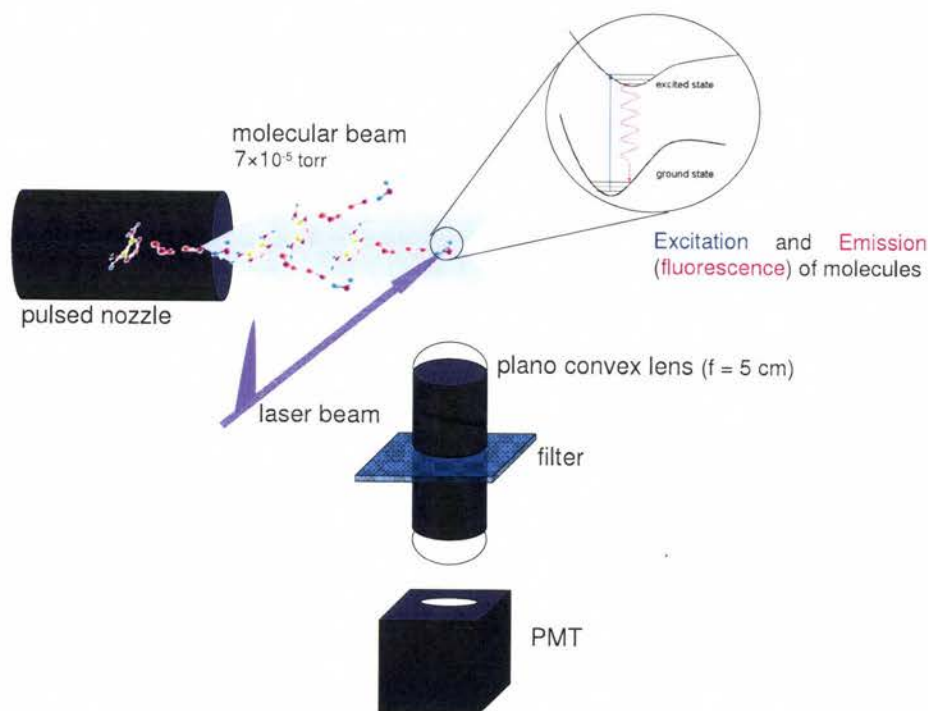


Figure 3: A general experimental scheme of LIF. Tunable laser light is passed through the molecular beam and any fluorescence produced is collected off-axis, at a right angle to the laser by a collection lens.

A number of radicals such as NO, NH₂, OH, CH₃O, and CH₃ generated due to decomposition of energetic systems are detected using LIF spectroscopy, which are discussed in different chapters in this thesis. The sample molecules are excited with 226

nm, and the decomposition product is detected using a second probe laser. The fluorescence light is detected by photomultiplier tube (PMT). When the probe laser is off resonance no fluorescence will be produced and the PMT will register no signal. However, when resonant fluorescence is possible, absorption can be registered by detecting emission from excited state. Therefore, a spectrum is obtained by measuring the fluorescence intensity as a function of laser wavelength.

4. Femtosecond Time Resolved Pump-Probe Spectroscopy

Femtosecond time resolved experiments involve a pump-probe configuration in which sample molecules are excited by the pump beam and dissociate according to their dissociation dynamics. Dissociation products are subsequently ionized by the time delayed probe beam and detected via TOFMS. By delaying the probe beam with respect to the pump beam, product appearance times can be determined. In the present experiments, two different pump-probe configurations are utilized: (1) a single laser beam at 226 nm is equally split into pump and probe beams; and (2) a pump pulse at 271 nm is used to excite the parent molecule and a probe pulse at 406.5 nm is used to ionize the molecule from its excited state. Here an example of the 2nd pump-probe configuration is considered to address experimental details of a generic femtosecond time resolved experiments and is illustrated in Figure 4. Further details can be found in Margo's thesis.⁴

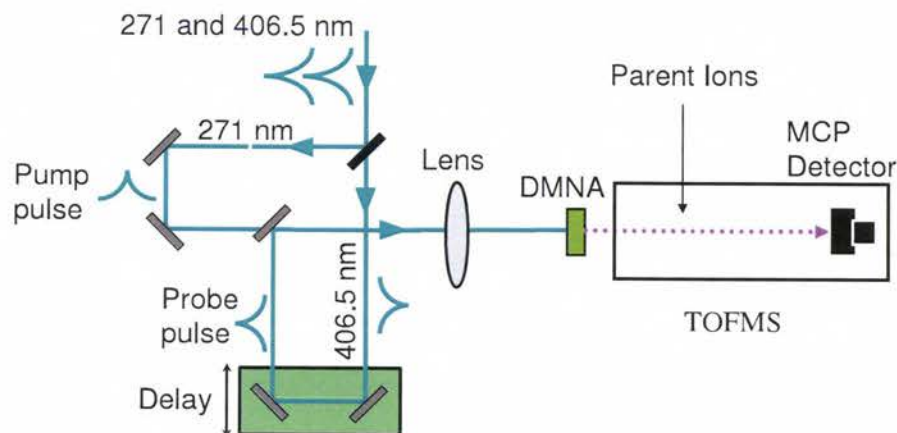


Figure 4: A generic femtosecond pump-probe experimental setup.

The fs laser light is generated by a femtosecond laser system consisting of a self-mode-locked Ti:Sapphire oscillator (KM Labs) and a home-made ring cavity Ti:Sapphire amplifier. The fs laser output (813 nm) is frequency doubled (406.5 nm) in a BBO crystal and then the fs laser fundamental output (813 nm) is mixed with doubled output (406.5 nm) in another BBO crystal to generate fs light at 271 nm. The pulse duration of both laser pulses at 271 and 406.5 nm are measured to be 170 fs using a off-resonance two-photon absorption of the benzene molecule. The pump and probe pulses follow different path before inducing variable delay line. The probe path length is changed by moving a motorized linear stage (Thorlabs). A retro-reflector (two-mirrors at 45° angles to each other) is positioned on a stepper motor controlled linear stage. As the stage is moved backwards, the probe beam follows a longer path length than the pump beam (see Figure 4). The linear stage can be moved in very small intervals (13 fs steps) giving high temporal resolution to the time evolution of some property of the system (decomposition product onset). It is important that the two beams, after following different optical paths, are directed and focused on the same spatial area in

the sample, taking care that the probe beam is always within the excitation beam. Temporal and spatial overlap between pump and probe can be easily found by looking at the two collinear beams for diffraction rings on a fluorescing business card. At zero time delay, when the spatial overlap is optimized, diffraction ring looks like a constructive/destructive interference pattern.

5. Control of Electronic Timing

Arrival times of different lasers (pump and probe), molecular beam, ablation laser must be temporarily synchronized to observe signal in TOFMS or LIF spectrometer. The timing in the present experiments is controlled by two SRS delay generators. The internal 10 Hz triggering system of one delay generator is used to externally trigger the second delay generator keeping them synchronized. These two synchronized SRS boxes are then used to externally trigger the rest of the equipment necessary for the experiment. An exemplary electronic triggering scheme which uses two dye lasers, a desorption laser, and supersonic pulsed nozzle is shown in Figure 5.

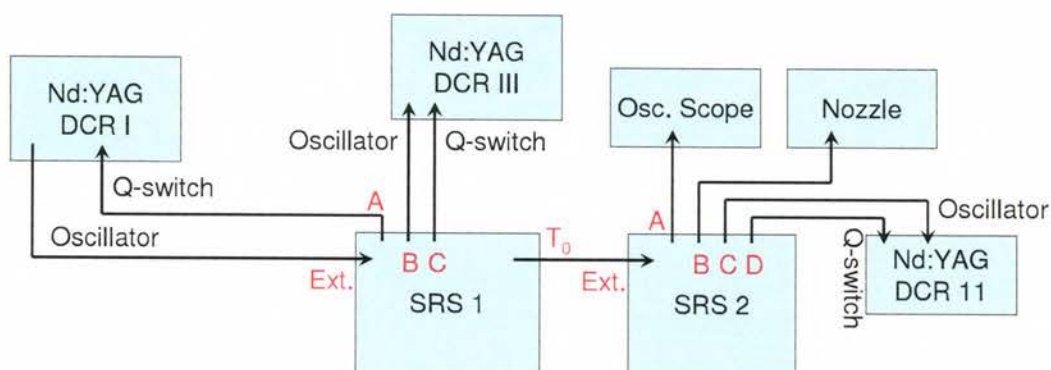


Figure 5: Electronic triggering scheme employing two dye lasers, nozzle, one ablation laser, and one oscilloscope.

The timing sequences are following:

SRS 1:

1) DCR I:

Q-switch: $A=T+3.582026\text{ ms}$ (50Ω , TTL, Normal)

2) DCR III:

Oscillator: $B=T+533.628\text{ }\mu\text{s}$ (High Z, TTL, Normal)

Q-switch: $C=B+3.0488\text{ ms}$ (50Ω , TTL, Normal)

SRS2:

1) Oscilloscope: $A=T+3.582488\text{ ms}$ (High Z, TTL, Normal)

2) Nozzle: $B=T+3.26635\text{ ms}$ (50Ω , TTL, Normal)

3) DCR 11:

Oscillator: $C=B-5.77\text{ }\mu\text{s}$ (High Z, TTL, Normal)

Q-switch: $D=C+250\text{ }\mu\text{s}$ (50Ω , TTL, Normal)

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APPENDIX II

Two Photon Spectroscopy of N₂: A Baby's Step to Study Decomposition of High Nitrogen Content Energetic Materials

Introduction

Nitrogen molecules are ubiquitous in combustion processes,¹ atmospheric phenomena,² and catalysis,³ and are expected to be major products from decomposition of high nitrogen content energetic materials. Consequently, methods for their detection have been explored for decades.⁴⁻¹⁸ State resolved and high sensitive detection of N₂, however, still poses a challenge because of a number of issues: (a) since N₂ is homonuclear diatomic molecule, direct infrared absorption is forbidden; (b) all electronic excited states of N₂ lie above ~6 eV, thus one-photon electronic absorption requires tunable vacuum ultraviolet radiation (VUV); and (c) the ionization potential of N₂ is very high (~15.6 eV).

A few spectroscopic probes that have been utilized in the past for the state-resolved detection of N₂ are Raman scattering,⁴ CARS,⁵ and electron excited fluorescence.⁶ Unfortunately, all of these techniques are hampered by poor detection sensitivity. Detection schemes that utilize an ionization probe of the resonant intermediate state (called as resonance enhanced multiphoton ionization, REMPI) enormously improve the detection sensitivity (~10⁵-10⁸ molecules/cm³) of N₂.⁷⁻¹⁸ The

additional benefits of the REMPI detection schemes are that they result in a simple, easily analyzable spectrum from which estimates of the rotational and vibrational populations of N₂ can be directly obtained. This combination of high sensitivity and spectroscopic simplicity makes the REMPI scheme a useful spectroscopic tool for the study of the decomposition of high nitrogen content energetic materials, and particularly to probe rotational and vibrational distributions of the N₂ product expected to be generated upon excited electronic state decomposition of the nitrogen rich compounds.

The present appendix discusses two REMPI schemes utilizing two different electronic transitions of N₂, which are employed for rovibrational-state resolved detection of N₂ in TOFMS: (1) (2+2) REMPI employing the $N_2^+ \leftarrow \tilde{a}^1\Pi_g \leftarrow \tilde{X}^1\Sigma_g^+$ electronic transition; and (2) (2+1) REMPI employing the $N_2^+ \leftarrow a''^1\Sigma_g^+ \leftarrow \tilde{X}^1\Sigma_g^+$ electronic transition. Subsequently, detection sensitivity of N₂ for these two REMPI techniques is determined for our TOFMS instrument. Knowledge of detection sensitivity is necessary to determine the yield of the N₂ product expected to be generated from decomposition of nitrogen rich compounds. This appendix also demonstrates successful employment of the (2+1) REMPI technique to detect N₂ product from excited electronic state decomposition of N₂O gas.

The (2+2) REMPI scheme requires four photons and the (2+1) REMPI requires three photons to ionize N₂ molecules. Due to the low intrinsic detection sensitivity of a four-photon ionization process over a three-photon process, the (2+1) REMPI scheme is found to have about three orders of magnitude higher N₂ detection sensitivity over that of the (2+2) REMPI scheme. Both (2+2) and (2+1) REMPI techniques, however,

can be potentially applied to study excited electronic state decomposition of high nitrogen content energetic materials in future. Rotational temperature of N₂ expanded directly from pulsed nozzle is estimated to be ~10 K using both techniques. Rotational temperature of the N₂ product from excited electronic state decomposition of N₂O, however, is found to be ~2000 K.

Experimental Procedure

The experimental setup consists of ns laser systems, a supersonic jet expansion pulsed nozzle, and a vacuum chamber for time of flight mass spectrometry, described in detail elsewhere.¹⁹⁻²³ Tunable radiation used to excite the (1,0) band of the two-photon $\tilde{a}^1\Pi_g \leftarrow \tilde{X}^1\Sigma_g^+$ transition in N₂ near 283 nm is generated by frequency doubling the output of a Nd:YAG pumped dye laser. The UV light is separated from the residual green fundamental by a Pellin-Broca prism. The dye laser is operated with a rhodamine 590 dye. Typical pulse energies are ~6 mJ/pulse at 283 nm, measured at the entrance of the TOFMS chamber. Since a multiphoton process in general requires a high photon density, the UV laser beam focused between the grids of a time-of-flight mass spectrometer ionization region by a 40 cm focal length lens.

Tunable radiation used to excite the (0,0) band of the two-photon $a''^1\Sigma_g^+ \leftarrow \tilde{X}^1\Sigma_g^+$ transition in N₂ near 203 nm is generated by frequency tripling the output of an Nd:YAG pumped dye laser. The dye laser output (~600 nm) is frequency doubled (~300 nm) in a KDP crystal, and then the dye laser output (~600 nm) is mixed with the frequency doubled output (~300 nm) in a BBO crystal. More detailed description for the generation of tunable 203 nm light is given in Appendix III. The dye laser is operated with a rhodamine 640 dye. Laser beam at 203 nm with an average

energy of 800 $\mu\text{J}/\text{pulse}$ is focused in the ionization region of a time-of-flight mass spectrometer by the 30 cm focal length lens.

The experiment is run at a repetition rate of 10 Hz. The timing sequence for the pulsed nozzle and ionization laser is controlled by a time delay generator (SRS DG535). A background pressure of 5×10^{-5} Torr is maintained in the vacuum chamber during the experiment. Ions are detected by a three plate microchannel plate detector (MCP). Signals are recorded and processed on a PC using a box car averager (SRS SR 250) and an ADC card (Analog Devices RTI-800).

Results and Discussions

The resonance transitions $\tilde{a}^1\Pi_g \leftarrow \tilde{X}^1\Sigma_g^+$ and $a''^1\Sigma_g^+ \leftarrow \tilde{X}^1\Sigma_g^+$ are essentially electric-dipole allowed two-photon transitions which are forbidden in one photon spectroscopy; specifically, $g \leftrightarrow g$, $u \leftrightarrow u$, $+\leftrightarrow+$, and $-\leftrightarrow-$ transitions. In principle, the selection rule for electric-dipole allowed two photon vibronic transitions is $\Delta J = 0, \pm 1, \pm 2$. Thus, the resonant state in REMPI scheme is restricted to being a singlet state with gerade inversion and positive reflection symmetries for two photon transitions because the ground state of N_2 is a singlet and has gerade inversion with positive reflection symmetry. Furthermore, since the $g \leftrightarrow u$ one-photon excitation selection rule is rigorously conserved in electronic transitions of homonuclear diatomic molecules, the virtual state symmetry for a $\tilde{a}^1\Pi_g \leftarrow \tilde{X}^1\Sigma_g^+$ and $a''^1\Sigma_g^+ \leftarrow \tilde{X}^1\Sigma_g^+$ two-photon transitions can only be a Π_u or a Σ_u state.

Detection of N_2 through (2+2) REMPI

Utilizing the two photon $\tilde{a}^1\Pi_g(v'=1) \leftarrow \tilde{X}^1\Sigma_g^+(v''=0)$ transition, less than 0.001% N_2 (10 ppm) in He can be detected with substantial signal to noise ratio. The (2+2) REMPI spectrum of N_2 from 1% N_2 in He gas mixture, observed around the (1,0) band head of a two photon $\tilde{a}^1\Pi_g(v'=1) \leftarrow \tilde{X}^1\Sigma_g^+(v''=0)$ electronic transition near 283 nm is shown in Figure 1. The most intense feature in the spectrum belongs to S-branch ($\Delta J = +2$) of the (1,0) band. This feature originates in the spectrum due to electronic transition from $J''=0$ level of the $\tilde{X}^1\Sigma_g^+$ ground electronic state of N_2 . Spectral features which appear blue to the most intense peak arise due to transitions from higher ($J'' > 0$) rotational levels and belong to the S-branch. Features which appear to the red of the most intense peak belong to Q- ($\Delta J = 0$) and R- branches ($\Delta J = +1$) of (1,0) band.

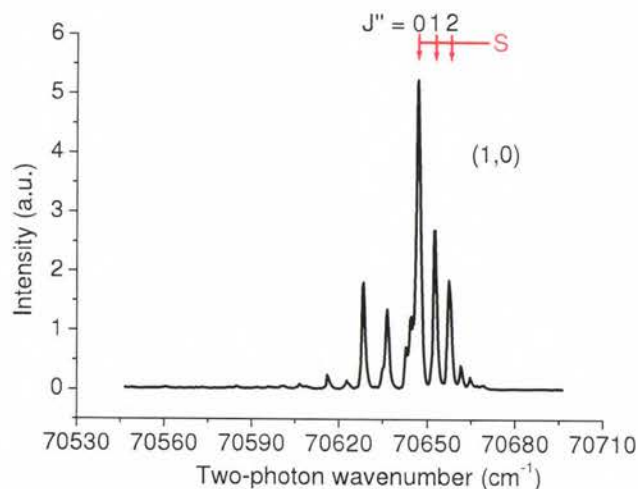


Figure 1: (2+2) REMPI spectrum of N_2 from 1% N_2 in He gas mixture, observed around (1,0) band head of $\tilde{a}^1\Pi_g(v'=1) \leftarrow \tilde{X}^1\Sigma_g^+(v''=0)$ electronic transition near 283 nm. Rotational temperature is estimated to be 10 K.

In one photon spectroscopy, when the rotational energy distribution follows the Boltzmann population distribution, the population $N(J)$ at the rotational level J is proportional to $(2J+1)\exp\left[-E_{rot}(J)/kT_{rot}\right]$, in which $E_{rot}(J)$ is rotational energy at J and T_{rot} is the rotational temperature. In two photon spectroscopy, however, the rotational line intensity is related to T_{rot} by following relationship:⁷

$$I_{J',J''} = Ag(J'')S(J',J'')\exp\left[-E_{rot}(J'')/kT_{rot}\right] \quad (1)$$

Here J' and J'' are the rotational quantum numbers of the resonant and ground state, respectively, A is a proportionality constant independent of rotational quantum numbers, $g(J'')$ is the nuclear spin statistical weight of nitrogen molecules, and $S(J',J'')$ is two-photon Hönl-London factors²⁴ of the $\tilde{a}^1\Pi_g \leftarrow \tilde{X}^1\Sigma_g^+$.

Table 1: Two-photon Hönl-London factors of N_2 for the $\tilde{a}^1\Pi_g \leftarrow \tilde{X}^1\Sigma_g^+$ transition using linearly polarized light.²⁴

Branch	$S(J',J'')$
O ($\Delta J = -2$)	$M(O)J''(J''-2)/15(2J''-1)$
P ($\Delta J = -1$)	$M(P)(J''+1)/30$
Q ($\Delta J = 0$)	$M(Q)(2J''+1)/10(2J''-1)(2J''+3)$
R ($\Delta J = +1$)	$M(R)J''/30$
S ($\Delta J = +2$)	$M(S)(J''+1)(J''+3)/15(2J''+3)$

The two-photon Hönl-London factors for the $\tilde{a}^1\Pi_g \leftarrow \tilde{X}^1\Sigma_g^+$ transition are shown in Table 1. The $M(O)-M(S)$ are the transition dipole factors given by products of the electronic dipole transition moments, and they depend on the rotational branch types. Generally, determination of the transition dipole moments theoretically for multiphoton transitions such as REMPI is difficult; however, they are independent of J ,

and thus they can be considered constants when the spectral lines of REMPI in the same branch are analyzed.

Utilizing equation (1), the rotational temperature T_{rot} can be deduced by a slope of Boltzmann plot of $\ln\left(\frac{I_{J',J''}}{g(J'')S(J',J'')}\right)$ versus $E_{rot}(J'')$.

$\ln\left(\frac{I_{J',J''}}{g(J'')S(J',J'')}\right)$ versus $E_{rot}(J'')$ plot for N_2 is illustrated in Figure 2. This gives a linear plot with a slope of -0.15 cm. From this measurement rotational temperature of N_2 is estimated to be ~10 K.

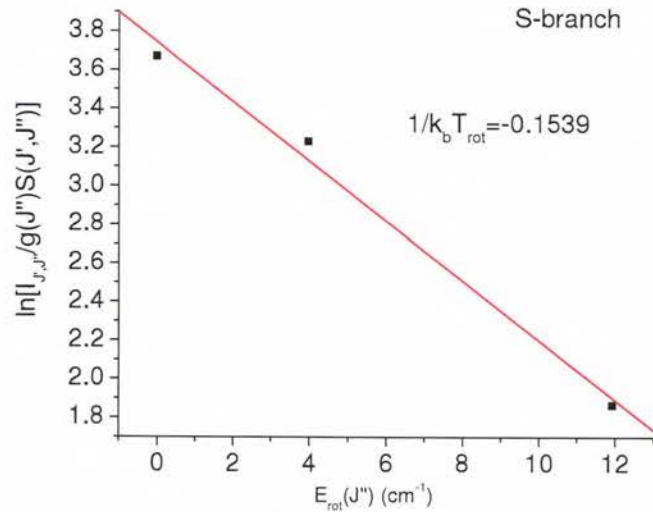


Figure 2. Boltzmann plot from signal amplitudes of the REMPI spectrum for the S-branch lines. From the slope from this plot, a rotational temperature of 10 K is estimated.

Detection of N_2 through (2+1) REMPI

Utilizing the two photon $a''^1\Sigma_g^+(v'=0) \leftarrow \tilde{X}^1\Sigma_g^+(v''=0)$ transition approximately 1-10 ppb N_2 in He can be detected with substantial signal to noise ratio. The (2+1) REMPI spectrum of N_2 observed around (0,0) band head of

$a''^1\Sigma_g^+(v'=0) \leftarrow \tilde{X}^1\Sigma_g^+(v''=0)$ electronic transition near 203 nm is shown in Figure 3. All of the spectral features in the spectrum belong to the Q-branch of the (0,0) band of the two-photon $a''^1\Sigma_g^+(v'=0) \leftarrow \tilde{X}^1\Sigma_g^+(v''=0)$ electronic transition of N_2 .

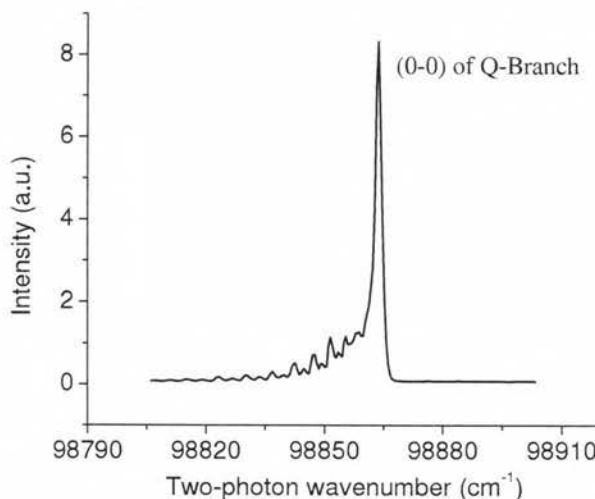


Figure 3: (2+1) REMPI spectrum of N_2 from 1% N_2 in He gas mixture, observed around (0,0) band head of $a''^1\Sigma_g^+(v'=0) \leftarrow \tilde{X}^1\Sigma_g^+(v''=0)$ electronic transition near 203 nm.

Detection of N_2 from photodissociation of N_2O at 203 nm

The N_2 product is detected from photodissociation of N_2O near 203 nm utilizing (2+1) REMPI employing the $N_2^+ \leftarrow a''^1\Sigma_g^+ \leftarrow \tilde{X}^1\Sigma_g^+$ electronic transition. The (2+1) REMPI spectrum of the product N_2 generated from photodissociation of N_2O near 203 nm is shown in Figure 4. The wavelength corresponds to both photodissociation and detection wavelengths. The 2:1 alteration of the intensities for the even-to-odd rotational lines arises from the Bose-Einstein nuclear spin statistics for $^{14}N_2$.²⁵ The rotational temperature is estimated to be ~ 2000 K, which indicates that photodissociation of N_2O at 203 nm generates rotationally very hot product N_2 .

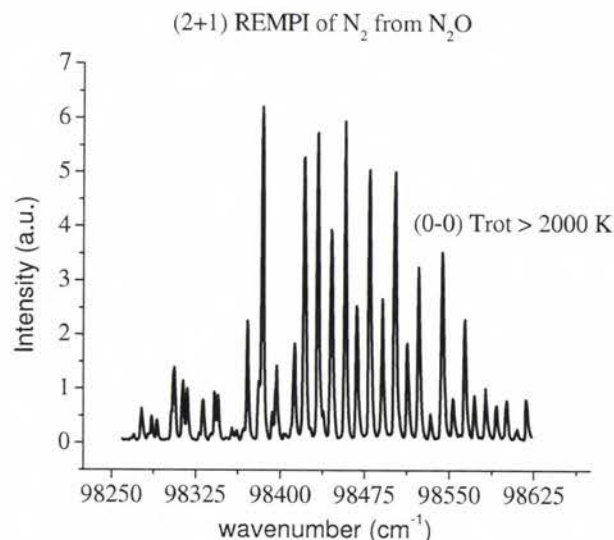


Figure 4: (2+1) REMPI spectrum of N_2 generated from the photodissociation of N_2O near 203 nm.

Conclusions

The detection of molecular nitrogen at high resolution and high sensitivity is of importance for the study of unimolecular decomposition of high nitrogen content energetic materials. This appendix discusses how to detect N_2 and what is the detection sensitivity for our instrument. (2+1) REMPI scheme is found to have about three orders of magnitude higher N_2 detection sensitivity over that of (2+2) REMPI scheme. Utilizing the (2+1) REMPI scheme, the N_2 product is detected following photodissociation of N_2O gas. REMPI techniques presented here can be used to study excited electronic state decomposition of high nitrogen content energetic materials. Further discussion of the detection of the N_2 product from high nitrogen content energetic materials can be found in Chapter 7.

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APPENDIX III

Generation of 200 nm Light with a BBO Crystal

Introduction:

Two photon transitions of some important atomic and molecular species such as molecular hydrogen, nitrogen, and oxygen fall near 200 nm region. Efficient generation of 200 nm light is therefore necessary to detect these species using optical spectroscopy. UV wavelength near 200 nm can be generated efficiently via third harmonic generation of a narrowband dye laser by mixing the output of the dye laser and its second harmonic using a β -BaB₂O₄ (BBO) nonlinear crystal.¹

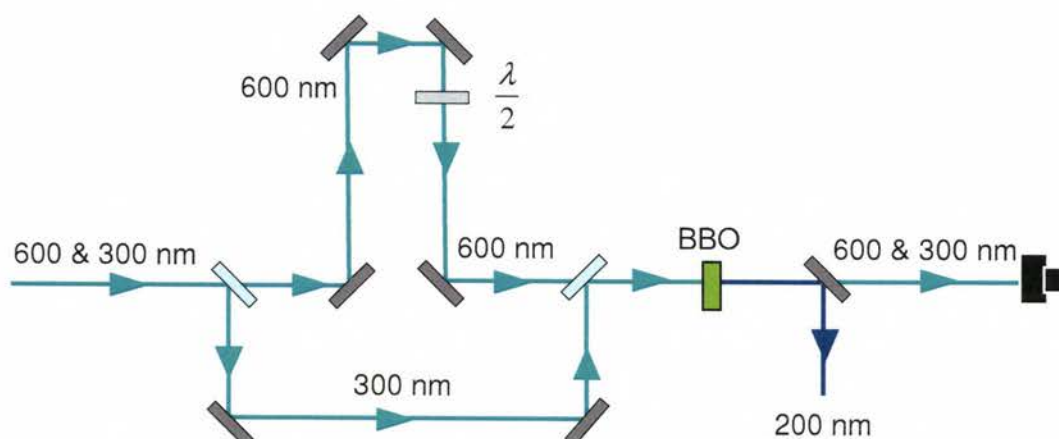


Figure 1. Schematic diagram of the laser setup used for generation of 200 nm laser beam

Experimental Setup:

The experimental arrangement for the generation of 203 nm light is illustrated in Figure 1. A dye laser pumped by the second harmonic output of a Nd:YAG laser is used to produce tunable light around 600 nm with an average energy of 10 mJ/pulse. The dye laser output is frequency doubled in a KDP crystal, resulting upto 6 mJ/pulse output energy which is tunable around 300 nm. This frequency doubled light (300 nm) is separated from the residual fundamental dye laser light (600 nm) by a dichoric mirror. A half wave plate ($\frac{\lambda}{2}$) is used to rotate the polarization of the visible light (near 600 nm) to match that of the UV (near 300 nm). The beams are then recombined with a dichoric mirror and directed collinearly into the BBO crystal (United Crystal). Typically both input beams have energy of 5 mJ/pulse.

The BBO crystal has dimensions of 6×6×10 mm and is cut at an angle of 78° with respect to its optic axis. The sum frequency output is separated by two dielectric coated mirrors (CVI) with a center wavelength of 203 nm.

Reference:

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APPENDIX IV

Computing Electronically Excited States

Introduction

Accurate calculation of excited electronic states has been a challenge for quantum chemistry. The possibility for accurate calculations of such states in molecules has only recently been made possible through the development of new quantum chemical techniques. Complete active space self consistent field (CASSCF)¹ calculation is currently one of the more successful methods to compute excited electronic states due to its balance between accuracy and cost. In addition to the intrinsic limitations of this method, photochemistry and photophysics involves a large number of situations and mechanisms which complicate the problems enormously. In the present appendix a systematic way is shown to deal with a large number of electronically excited states of a molecule. We have selected examples of two energetic model systems DMNA and furazan: our goal is to compute and identify their electronically excited states at their ground state geometry. This computation is able to estimate vertical excitation energies for different electronically excited states which can be viewed as the absorption maxima in the gas phase absorption spectrum of the molecule. The calculations comprise an extensive use of the CASSCF and CASMP2 methodologies using Gaussian 03² and Molpro.³ Selection of proper active space with

specific examples, identification of the nature of excited state, calculations of vertical excitation energies, incorporation of dynamical correlation energies to the computed excited state energies will be some of the topics covered.

Theoretical Background

The complete active space self consistent field (CASSCF) method is a commonly used kind of multiconfiguration SCF (MCSCF) method. In the MCSCF method, molecular wavefunction is written as a linear combination of configuration state functions (CSFs, Φ_i):

$$\Psi = \sum_i b_i \Phi_i \quad (\text{a})$$

Configuration state functions (Φ_i) are formed using molecular orbitals (ϕ_i):

$$\Phi_i = \prod_i \phi_i \quad (\text{b})$$

The molecular orbitals used to construct CSFs are formed as linear combinations of basis functions (χ_r):

$$\phi_i = \sum_{r=1}^N c_{ri} \chi_r \quad (\text{c})$$

In the CASSCF methodology, the molecular orbitals (ϕ_i) are divided in inactive and active orbitals. The inactive orbitals are kept doubly occupied in all CSFs. The electrons not in the inactive orbitals are called active electrons. The CASSCF wavefunction is then written as a linear combination of all CSFs (Φ_i) that can be formed distributing the active electrons among the active molecular orbitals in all possible ways. The CSFs must have the same spin and symmetry eigenvalues as the states to be treated at the CASSCF level. Subsequently, the variation method is applied

to find the optimum coefficients c_{ri} and b_i . A reasonable choice is to take the active orbitals as those molecular orbitals (ϕ_i) that arise from the valence orbitals of the atoms that form the molecules such as nonbonding orbitals, π orbitals, etc.

The Vertical Excitation Energies

Electronic excitation promotes a molecule from its ground to an excited electronic state. Electronic excitation takes place so fast that the nuclei do not have enough time to move. Thus the positions of the nuclei in the excited electronic state are identical to those in the ground state (Franck-Condon rule). The quantum mechanical interpretation of the Franck-Condon rule is that the probability of the nuclei making a transition from one potential energy surface to another is greatest for those places at which the square of the overlap between the vibrational wavefunction of the initial and final states $q_{v',v''} \equiv |\langle \psi_{v'}(R) | \psi_{v''}(R) \rangle|^2$, called Franck-Condon factor, is the greatest. Thus following electronic excitation, the molecule undergoes a vertical transition in the coordinate space. Vertical excitation energies can be computed at the CASSCF level of theory utilizing the ground state geometry of the molecule.

The CASSCF method has the basic limitation of the size and selection of the active space in the preliminary step, not only because the space cannot be too large, but because the active space defines the type and number of configurations to be identified in the total CASSCF wave functions. The near-degenerate configurations describing all states must be present in the total wave function. Therefore, certain knowledge of the system is necessary to design the calculation to estimate the vertical excitation energies. For excited state computations, this requirement of chemical knowledge will limit the number of states we are able to study.

CASE STUDY I: DMNA:⁴ Gaussian Example

Steps Necessary to Estimate Vertical Excitation Energies:

The method can be broken down into several steps (see Gaussian 03 manual for details):

- ❖ Perform a population analysis calculation at RHF for closed shell system or at UHF level for open shell system.

For closed shell system Pop = Full is included to obtain the canonical orbitals.

For an open shell system Pop = NaturalOrbitals is included to obtain the natural orbitals. The basis set needs to be used in this step is STO-3G. STO-3G is a minimal basis set, which is not perfect to get accurate energy; however, it does not possess diffuse functions and therefore, molecular orbitals obtained using this basis set can be very easily judged to determine the correct orbitals needed to be included in the active space.

- ❖ Run CASSCF calculation for ground state using *NRoot* = 1 option.

If the initial guess of the orbitals from RHF or UHF is in correct order, CASSCF calculation can be performed using Guess=Read keyword. On the other hand, if the initial guess from RHF/UHF calculations is not in correct order, correct orbitals can be moved into the active space using Guess=Alter keyword.

- ❖ Run CASSCF calculation at excited state using *NRoot* = $n(n = 2, 3, \dots)$ option.

*A state-averaged CAS calculation for the excited state of interest (as specified by the *NRoot* option) can be performed using StateAverage option. This state-averaged CAS calculation requires weight for each state, which needs to be*

specified in a separate input section. Sometimes, single root calculation for the excited states does not converge because of root flopping or other numerical problems. Furthermore, if single root option is used, the energy of the respective root gets biased to that root, predicting wrong energy for that root. One way to circumvent this problem is to minimize average energy of a number of states together using StateAverage option.

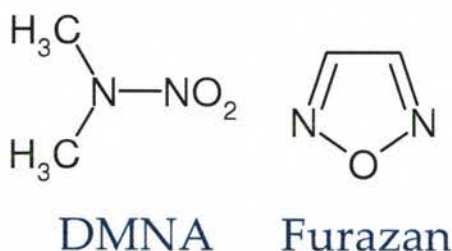


Figure 1: Chemical structures of DMNA and furazan

Planning the Calculation:

DMNA is a nitramine molecule with a planar N-NO₂ energetic moiety. Structure of DMNA illustrated in Figure 1. Preliminary chemical knowledge and intuition suggests that the π system of DMNA contains delocalized double bonds on the NO₂ moiety. Therefore, the π valence molecular orbitals are one delocalized bonding π_{NO_2} , one nonbonding $n\pi_o$ orbital placed on the oxygen atoms and one antibonding $\pi_{NO_2}^*$. The $\pi_{NO_2}^*$ orbital should be the lowest unoccupied molecular orbital in this system. The highest occupied molecular orbital, however, should be the nonbonding orbital $n\sigma_o$ which is co-planar with the σ skeleton of the N-NO₂ moiety. Thus, electronic excitation from this nonbonding orbital $n\sigma_o$ to the lowest unoccupied

molecular orbital $\pi_{NO_2}^*$ should form the first excited electronic state. This electronic transition should contribute to the UV spectrum in gas phase. Other orbitals involved in other low lying excited electronic states should be the nonbonding $n\pi_o$ and bonding π_{NO_2} .

With this in mind we have to include at least all the π valence orbitals (including bonding and antibonding) and the $n\sigma_o$ valence nonbonding orbitals on the oxygen atoms in the active space. This minimum valence active space of DMNA can be labeled as (6e,4o), where 6 electrons (doubly occupied $\pi_{NO_2}, n\pi_o, n\sigma_o$) are distributed in 4 orbitals ($\pi_{NO_2}, n\pi_o, n\sigma_o, \pi_{NO_2}^*$). However, these are not the only molecular orbitals (ϕ_i) which construct CSFs for DMNA in order to express its total CASSCF wavefunction. A number of σ valence bonding orbitals forming N-N and N-O bonds can participate in CSFs for low lying excited electronic states of DMNA. Chemical knowledge gleaned from experimental observation on excited electronic state decomposition of DMNA is here necessary to decide whether these σ valence bonding orbitals forming N-N and N-O bonds must be simultaneously included in the calculation. Final selection of optimum active space which balances cost and accuracy, therefore, depends on many factors including some chemical knowledge/intuition for the system of interest.

Experimental observations indicate that the low lying excited electronic state (of $(n \rightarrow \pi^*)$ or $(\pi \rightarrow \pi^*)$ character) decomposition of DMNA happens though nitro-nitrite isomerization:



In this reaction, simultaneously the N-N bond dissociates and the N-O bond forms. These N-N and N-O σ bonds, therefore, are chemically important and need to be included in the active space for calculation of low lying excited electronic states of DMNA. Thus, the optimum active space for DMNA to explore low lying excited states is labeled as (14,11), where 14 electrons (from doubly occupied $2\sigma_{NO}, \sigma_{NN}, \pi_{NO_2}, n\pi_O, 2n\sigma_O$) are distributed in 11 orbital ($2\sigma_{NO}, \sigma_{NN}, \pi_{NO_2}, n\pi_O, 2n\sigma_O, 2\sigma_{NO}^*, \sigma_{NN}^*, \pi_{NO_2}^*$). One of the σ_{NO} orbital has mostly $2S_N$ character and according the calculations done by Soto et al.⁵ that σ_{NO} is named as $2S_N$. All the molecular orbitals selected for the active space of DMAN, calculated at CASSCF(14,11)/STO-3G level of theory is illustrated in Figure 2.

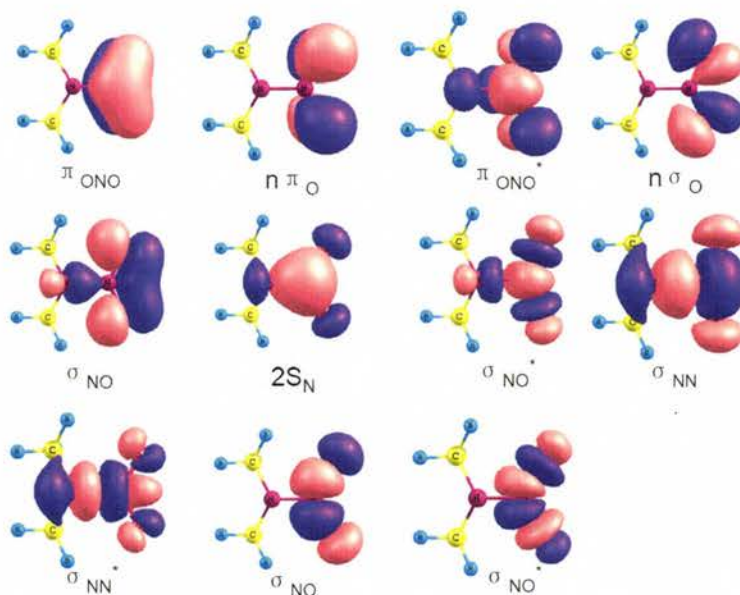


Figure 2: Active orbitals used for (14,11) active space of DMAN computed at CASSCF(14,11)/6-31G(d) level of theory.

Once an active space is roughly surmised using either chemical intuition or experimental justification, we can use the active space and run a series of calculations

to determine the nature of the excited state and determine the excitation energies. Fidelity of the active space can be judged comparing experimental absorption spectra with the computed vertical excitation energies. The following sections describe the use of Gaussian 03 discussing the input file to run those calculations and explaining the output files to interpret the theoretical results.

Utilizing Gaussian 03 the number of electrons (e) and number of orbitals (o) in the active space for a CASSCF calculation is specified following the keyword: *CASSCF(e,o)*. By default, the active space is defined assuming the electrons come from the highest occupied orbitals in the initial gauss and that the remaining orbitals required for the active space come from the lowest virtual orbitals of the initial gauss. Thus, for a *CASSCF(14,11)* calculation on a closed shell system, the active space consists of:

1. Enough occupied orbitals to form the initial guess to provide 14 electrons. Thus the 7 chemically important occupied orbitals need to be included.
2. Enough virtual orbitals to make a total of 11 orbitals. Since 4 unoccupied orbitals were already included, 2 virtual orbitals would become part of the active space.

Performing CASSCF calculation

Here are the input files for the CASSCF calculation of DMNA using (14,11) active space:

Preliminary examination of the orbitals

(taken from the pop.log file)

```
%mem=600MB
%chk=pop
#p RHF/STO-3G Pop=Full Gfinput NoSymm
```


Population analysis of DMNA

0	1		
7	0.000000000	0.522634000	-0.377494000
7	0.000000000	-0.300911000	0.741565000
8	1.105885000	-0.613949000	1.209350000
8	-1.105885000	-0.613949000	1.209350000
6	1.252121000	0.494867000	-1.126963000
6	-1.252121000	0.494867000	-1.126963000
1	1.150008000	1.214718000	-1.939372000
1	2.069816000	0.795380000	-0.476177000
1	1.464537000	-0.499731000	-1.537919000
1	-1.150008000	1.214718000	-1.939372000
1	-2.069816000	0.795380000	-0.476177000
1	-1.464537000	-0.499731000	-1.537919000

Here are the selected orbitals from the converged wavefunction from the

Pop = Full job (taken from the pop.log file)

Population analysis using the SCF density.

Molecular Orbital Coefficients

		21	22	23	24	25
		O	O	O	O	V
EIGENVALUES --		-.36842	-.35232	-.33509	-.28490	.22779
1 1 N 1S		-.05180	.00000	-.02563	.00000	.02021
2 2S		.25975	.00000	.13333	.00000	-.11964
3 2PX		.00000	-.02689	.00000	.00532	.00000
4 2PY		.21444	.00000	.73405	.00000	-.24056
5 2PZ		.43815	.00000	.18360	.00000	-.06301
6 2 N 1S		.01561	.00000	.00082	.00000	.00224
7 2S		-.07600	.00000	-.00156	.00000	-.01700
8 2PX		.00000	-.09787	.00000	-.00092	.00000
9 2PY		-.01912	.00000	-.11965	.00000	.62126
10 2PZ		-.11621	.00000	.05846	.00000	.42926
11 3 O 1S		-.01163	-.00945	.00553	-.00037	.00025
12 2S		.06131	.05481	-.03033	.00157	-.00067
13 2PX		-.09858	.46763	.05601	.00857	-.00701
14 2PY		-.41211	.28729	.02616	.59359	-.48994
15 2PZ		.37187	-.44903	-.39592	.38854	-.32630
16 4 O 1S		-.01163	.00945	.00553	.00037	.00025
17 2S		.06131	-.05481	-.03033	-.00157	-.00067
18 2PX		.09858	.46763	-.05601	.00857	.00701
19 2PY		-.41211	-.28729	.02616	-.59359	-.48994
20 2PZ		.37187	.44903	-.39592	-.38854	-.32630
21 5 C 1S		.00945	.00710	.00720	-.00017	-.01189
22 2S		-.04150	-.02630	-.02416	-.00124	.05792
23 2PX		.10097	-.02739	-.01155	-.00239	-.06425
24 2PY		-.03829	.00834	-.10889	-.01594	-.02480
25 2PZ		-.11231	-.04776	-.04582	-.01134	.03091
26 6 C 1S		.00945	-.00710	.00720	.00017	-.01189
27 2S		-.04150	.02630	-.02416	.00124	.05792
28 2PX		-.10097	-.02739	.01155	-.00239	.06425
29 2PY		-.03829	-.00834	-.10889	.01594	-.02480
30 2PZ		-.11231	.04776	-.04582	.01134	.03091
31 7 H 1S		.02907	.05372	-.07702	-.00921	.01313
32 8 H 1S		-.07058	-.02944	-.10992	.00091	.02836
33 9 H 1S		.12506	-.00688	.20277	.01311	-.07463

34 10 H 1S	.02907	-.05372	-.07702	.00921	.01313
35 11 H 1S	-.07058	.02944	-.10992	-.00091	.02836
36 12 H 1S	.12506	.00688	.20277	-.01311	-.07463

The (14,11) active space should contain 7 occupied orbitals (O) and 4 virtual orbitals (V). $2S_N$, σ_{NO} , σ_{NN} , π_{NO_2} , $n\pi_O$, $2n\sigma_O$, $2\sigma_{NO}^*$, σ_{NN}^* , and $\pi_{NO_2}^*$ are the chemically relevant orbitals we want to include to calculate CASSCF energy. As always, however, we must examine the relevant MOs obtained from single point RHF calculation to ensure that they are what and where we expect them to be. One way to judge the MOs is to look at the population analysis output file and look at the eigen values for each MO and coefficients for individual atomic orbitals contributing to the MO. For instance, let's judge occupied MO no. 24 and virtual MO no. 25 from the above population analysis result. MO no. 24 has an eigen value of -.28490 Hartree (1 Hartree = 27.2116 eV) and has large coefficients for $2p_y$ on the oxygen atoms and no large coefficients elsewhere, so this is the orbitals corresponding to nonbonding $n\pi_O$. We want to retain this orbital in the active space. Similarly, MO no. 25 has large positive coefficient for $2p_y$ on the nitrogen atom, and large negative coefficient for $2p_y$ on the oxygen atoms of the NO_2 group. Therefore, this MO belongs to antibonding $\pi_{NO_2}^*$, and we want to retain this orbitals in the active space.

Inspection of correct MOs, however, can be easily done using a visualization software such as ChemCraft. Figure 2 shows the molecular orbitals plotted utilizing ChemCraft from the population analysis output file obtained using CASSCF(14,11)/STO-3G level of theory.

CASSCF calculation

Population analysis at RHF/STO-3G level of theory predicts that MO no. 25 is the lowest unoccupied molecular orbital (LUMO) which is an antibonding $\pi_{NO_2}^*$ orbital. MO no. 26 is σ_{NN}^* , but MO no. 27 and 28 do not correspond to two σ_{NO}^* antibonding orbitals. If (14,11) active space is used, by default, $(11 - \frac{14}{2}) = 4$ lowest unoccupied orbitals will be used. First, two lowest antibonding orbitals are appropriate for the active space, but next two lowest unoccupied orbitals are not suitable for the active space. MO no. 36 and 33 correspond to the σ_{NO}^* antibonding orbitals obtained at RHF/STO-3G level. Therefore, to define the correct active space, orbitals 27 and 33 need to be swapped. Simultaneously, orbitals 28 and 36 need to be exchanged. This swapping of orbitals can be done using *Guess = Alter* keyword in a CASSCF calculation. As we need to use the initial guess from previous RHF/STO-3G calculation, a new checkpoint file *excite* is created copying from previous checkpoint file *pop*.

Here is the input file for the CASSCF calculation:

(taken from the excite.com file)

```
%chk=excite
%mem=600MB
#p CASSCF(14,11,NRoot=1)/STO-3G Guess=Alter Pop=Full NoSymm Gfinput
```

CASSCF calculation of DMNA

0	1		
7	0.000000000	0.522634000	-0.377494000
7	0.000000000	-0.300911000	0.741565000
8	1.105885000	-0.613949000	1.209350000
8	-1.105885000	-0.613949000	1.209350000
6	1.252121000	0.494867000	-1.126963000
6	-1.252121000	0.494867000	-1.126963000
1	1.150008000	1.214718000	-1.939372000
1	2.069816000	0.795380000	-0.476177000
1	1.464537000	-0.499731000	-1.537919000
1	-1.150008000	1.214718000	-1.939372000
1	-2.069816000	0.795380000	-0.476177000
1	-1.464537000	-0.499731000	-1.537919000

27,33

The output file of the calculation is following:

(taken from the excite.log file)

```
( 1) EIGENVALUE  -33345264E+03
(1) .9218600 (21) -.3179670 (190) -.0621487 (703) -.0609807 (3) -.0506685 (22157) .0448461 (722) .0430338
(8134) .0417743 (2558) -.0410962 (9317) .0365251 (171) -.0351082 (759) .0332103 (741) -.0317001
(22403) .0316647 (2776) -.0312253 (3246) -.0309240 (22616) -.0300134 (22385) .0292142 (22597) .0277864
(740) .0269188 (22227) .0255278 (22578) -.0255016 (175) .0254613 (669) .0249196 (6) -.0238544 (22366) -
.0232792 (707) -.0230862 (9318) .0221597 (406) .0214608 (1081) .0209892 (22192) .0207735 (8521) .0206804
(22582) -.0200063 (158) .0193645 (2628) -.0190505 (174) .0189535 (22809) .0189271 (2522) -.0183432
(22808) .0174156 (22791) -.0170444 (30877) .0169962 ( 2556) -.0160424 (170) -.0154333 (22581) -.0153521
(1109) -.0150694 (22369) -.0143098 (2575) .0142224 (22370) -.0139757 (5566) .0137947 (10) -.0137273
```

MCSCF converged.

The eigen value (-333.45264) corresponds to the ground state (as specified by $NR_{root}=1$) energy of the molecule at CASSCF(14,11)/STO-3G level of theory. Decimal numbers correspond to the coefficient of each CSF used to construct the total CASSCF wavefunction. Each CSF is defined by an integer number given within the bracket, preceding the decimal number. Meaning of the number which defines the CSF is discussed later in this appendix. Note that 14 electrons are distributed randomly in 11 orbitals to construct CSFs. In the present example, (14,11) active space generates more than 22,000 CSFs. Each CSF can be found in the output file of CASSCF job.

The above calculation shows that CSF no. 1 has largest coefficient (0.9218600). CSF no. 1 is defined as ground state configuration where no electronic excitation is considered and for a closed shell system like DMNA, occupied orbitals are doubly filled. Before proceeding to further calculation on excited electronic states, the active space must be rechecked. Figure 2 shows the active space obtained at CASSCF(14,11)/STO-3G level of theory. If the orbitals in the active space are of the correct nature, we can proceed further to next set of calculations. Otherwise, we need to bring the correct orbitals to the active space using *Guess = Alter* keyword and run the

CASSCF calculation once again. Once the correct active space is defined, one can improve the basis set in the following sequence: STO-3G, 4-31G, 6-31G(d), 6-31+G(d,p), and etc.

CASSCF vertical excitation energies

Vertical excitation energies can be computed using the $NRoot = n(n = 2, 3, \dots)$ keyword. Thus, if 1st singlet excited state energy needs to be computed, *CASSCF(14,11,NRoot = 2,StateAverage)/6-31G(d)* is used. Generally when different roots are computed simultaneously, it is convenient to use state-averaged calculation giving equal weight to the each root. This can be done using *StateAverage* keyword. State averaged calculation minimizes the average energy of different electronic states, and thus total wavefunction does not get biased to a particular state.

Here is the input file for the CASSCF calculation.

(taken from the excite1.com file)

```
%mem=200MB
%chk=excite1.chk
#p CASSCF(14,11,NRoot=3,StateAverage)/6-31G* Geom=Check
Guess=Read Pop=Full Ginput SCF=(MaxCycle=200) NoSymm
```

Excitation of FC geom of DMNA

```
0      1
7      0.000000000  0.522634000 -0.377494000
7      0.000000000 -0.300911000  0.741565000
8      1.105885000 -0.613949000  1.209350000
8     -1.105885000 -0.613949000  1.209350000
6      1.252121000  0.494867000 -1.126963000
6     -1.252121000  0.494867000 -1.126963000
1      1.150008000  1.214718000 -1.939372000
1      2.069816000  0.795380000 -0.476177000
1      1.464537000 -0.499731000 -1.537919000
1     -1.150008000  1.214718000 -1.939372000
1     -2.069816000  0.795380000 -0.476177000
1     -1.464537000 -0.499731000 -1.537919000
```

```
0.3333333 0.3333333 0.3333333
```

Here vertical excitation energies for two singlet excited states are computed giving equal weight (0.3333333) to the ground state and excited states.

The output file for this calculation:

(taken from the excite1.log file)

```
(1) EIGENVALUE -.33786773E+03
(1) .9412686 (136) -.1601049 (2486) .1035018 (2556) -.0747040 (8272) .0642341 (8456) .0611467
(10879) .0541837 (8515) -.0500945 (128) .0490079 (22649) .0461913 ( 8386) -.0444029 (17021) .0440963
(22403) .0419464 (352) -.0416253 (22708) -.0415822 (125) -.0407412 (703) -.0377976 (22578) -.0376555
(127) .0373101 (22791) -.0371831 (232) .0348513 (22369) .0337524 (2523) .0332434 (8385) -.0323998 (326) -
.0321570 (22807) .0315661 (22579) -.0309541 (2522) -.0302158 (6) -.0298122 (35779) .0297953 (669) -.0282080
(8423) -.0281973 (8422) .0279179 (22920) -.0272600 (22616) -.0271606 (27029) .0266246 (8261) .0259694
(8264) -.0257246 (36) -.0247419 (2664) .0245335 (9731) -.0212914 (2592) -.0205234 (666) -.0203089 (2776) -
.0201656 (2488) .0196088 (2701) -.0186938 (9181) -.0184453 ( 8263) -.0183341 (22581) -.0181739 ( 8295) -
.0180852
(2) EIGENVALUE -.33769240E+03
(16) .9323419 (122) -.2321824 (2491) -.0732370 (8258) .0569716 (22171) -.0524498 (9721) -.0509288
(30) .0476661 (9662) .0452060 (8647) .0450574 (12) -.0422457 (24744) -.0414040 (22163) .0411310
(24602) .0406773 (1072) -.0396741 (56) .0368373 (24522) -.0365201 (23) .0356020 (23437) .0348588
(17026) .0345880 (9582) -.0328095 (22717) -.0313566 (24347) .0313342 (24661) -.0312927 (22412) .0304988
(638) .0292367 (22793) .0271233 (8391) .0269136 (48) .0268819 (35784) .0262890 (9469) .0260397 (2495) -
.0253264 (637) -.0253136 (22584) .0249504 (2532) .0249075 (22284) .0238201 (2531) -.0222160 (9629) -
.0216639 (22376) -.0215965 (43661) -.0215931 (24569) -.0215726 (8010) .0211649 (132) .0211273
(10884) .0209470 (22162) .0208909 (8268) -.0207157 (22625) -.0206741 (18) .0203826 (9628) .0202495
( 676) .0201527 ( 8432) -.0200423
(3) EIGENVALUE -.33766180E+03
(2) .9206701 (126) -.2754015 (8262) .0573716 (8017) .0572861 (9454) .0571500 (34) .0543048 (8908) -
.0508302 (8849) .0493767 (27) .0469251 (633) -.0449069 (817) -.0403689 (20) -.0394810 (23433) -.0389750
(17022) .0368572 (23291) .0367846 (23217) -.0361783 (8006) .0342643 (2487) -.0331652 (634) .0322533 (8775)
-.0316568 (23350) -.0312001 (23042) .0311980 (22711) -.0311061 (22406) .0302346 (22158) .0289806
(67) .0288654 (35780) .0277050 (22797) .0275260 (8662) .0260269 (668) -.0259507 (63) -.0255039
(130) .0252414 (2526) .0250599 (131) .0223800 (8816) -.0223208 (9524) -.0222414 (2525) -.0218582
(8815) .0215245 (11032) -.0212908 (22368) .0210765 (8383) -.0208266 (23258) -.0206022 (24754) .0205860
(26802) -.0205386 (8267) -.0204090 (43957) -.0201962 (23008) .0200696 (8426) -.0196345 (8425) .0195917
(22619) -.0191511
```

The vertical excitation energy for the S_2 state is calculated to be 5.8 eV { (337.86773-337.66180)*Hartree* }. The vertical excitation energy for S_1 state is calculated to be 4.77 eV { (337.86773-337.6924)*Hartree* }.

Characterization of the Excited States

When we compute the vertical excitation energy of a particular excited electronic state, characterization of the respective state is absolutely necessary because that gives an idea about electronic excitation responsible to generate that excited

electronic state. For instance, if one π -electron is excited to a π^* antibonding orbital, the generated excited electronic state is characterized as (π, π^*) one. Characterization of an excited electronic state is done by inspecting the nature of CSF with highest coefficient for that state. The actual procedure is discussed below by taking an example of DMNA at CASSCF(10,7)/6-31G(d) level of theory. A reduced active space is used here including $2n\sigma_O$, $n\pi_O$, π_{ONO} , σ_{NN} , σ_{NN}^* , and π_{ONO}^* .

Here is the input file for the CASSCF calculation:

(taken from the excite.com file)

```
%mem=200MB
%chk=excit.chk
#p CASSCF(10,7,NRoot=3,StateAverage)/6-31G*
Guess=Read Pop=Full Ginput NoSymm SCF=(MaxCycles=300)
```

Excitation of FC geom of DMNA

```
0      1
7      0.000000000  0.606152000 -0.358763000
7      -0.000001000 -0.292338000  0.786631000
8      1.091020000 -0.609441000  1.237397000
8      -1.091022000 -0.609439000  1.237398000
6      1.226870000  0.494013000 -1.131766000
6      -1.226869000  0.494012000 -1.131766000
1      1.169349000  1.230610000 -1.920793000
1      2.078358000  0.720773000 -0.512500000
1      1.357871000 -0.490712000 -1.575317000
1      -1.169348000  1.230606000 -1.920796000
1      -2.078357000  0.720774000 -0.512501000
1      -1.357871000 -0.490715000 -1.575314000
```

```
0.3333333 0.3333333 0.3333333
```

The initial guess for this CASSCF calculation is generated from a RHF calculation following the procedure described above. Here, vertical excitation energies for two singlet excited states (using $NRoot=3$ keyword) are computed giving equal weight (0.3333333) to the ground state and excited states.

The output file for this calculation:

(taken from the excite.log file)

(1) EIGENVALUE -.33775587E+03
 (1) .9565832 (26) -.2193421 (91) -.0828430 (23) .0816392 (89) -.0794390 (47) -.0580829 (90) .0510222 (38) -.0503034 (13) -.0376438 (28) .0343203 (108) -.0336597 (24) -.0310819 (51) .0275801 (115) .0263343 (186) .0204607 (57) -.0167544 (118) -.0149746 (156) -.0132413 (177) .0124058 (53) -.0119354 (46) -.0104007 (174) -.0101524 (196) .0091674 (10) -.0091366 (32) .0085047 (127) -.0083696 (5) .0081416 (68) .0064599 (29) -.0064393 (7) .0058506 (97) .0045276 (61) .0044610 (84) -.0044315 (3) -.0041000 (159) .0038285 (17) -.0037594 (152) .0037270 (189) .0036849 (2) .0036197 (72) .0034451 (153) .0032130 (128) .0029176 (124) -.0027594 (56) .0027438 (184) -.0023998 (92) .0020347 (129) .0019358 (96) -.0019287 (121) -.0018917 (192) .0018863

(2) EIGENVALUE -.33758755E+03
 (4) .9321483 (11) .3190771 (132) -.0844256 (41) -.0744537 (86) -.0430124 (12) -.0427395 (39) -.0415586 (130) .0402598 (42) .0371393 (35) .0332343 (79) .0322593 (80) .0317068 (142) -.0314835 (166) -.0310646 (87) .0270413 (85) -.0226522 (16) -.0198252 (52) -.0186590 (116) .0131188 (34) .0126837 (8) -.0106280 (120) .0102980 (78) -.0094510 (160) -.0073839 (6) .0068485 (33) -.0065940 (133) .0059022 (59) .0058676 (67) .0054540 (171) .0054304 (191) -.0051550 (60) -.0049370 (15) .0046860 (125) -.0044542 (22) -.0041307 (62) -.0036699 (21) .0031166 (114) -.0027646 (107) .0027553 (182) -.0026802 (70) .0025608 (9) -.0025318 (113) .0024673 (54) .0020619 (27) .0017127 (55) -.0017040 (73) .0016519 (49) -.0015701 (75) -.0015111 (162) .0014661

(3) EIGENVALUE -.33756158E+03
 (2) .9167134 (17) .3638247 (112) -.0850364 (32) .0734148 (18) -.0518358 (44) .0392409 (111) .0355675 (178) -.0345933 (66) -.0341778 (126) -.0312449 (37) -.0284811 (103) .0281366 (31) -.0261822 (7) .0222476 (65) .0218344 (100) -.0211718 (143) .0205656 (72) .0163008 (50) -.0141370 (45) -.0121608 (64) -.0113258 (10) .0104357 (137) .0097871 (14) -.0086416 (145) -.0080644 (71) .0078847 (5) .0066612 (43) -.0065529 (40) -.0063091 (82) -.0062056 (102) .0061297 (47) .0059274 (3) -.0052937 (141) -.0050303 (19) -.0049987 (36) .0048816 (24) .0047458 (140) -.0046327 (13) .0044567 (175) .0044306 (147) -.0032845 (92) .0030206 (135) -.0029986 (188) -.0029929 (124) .0029665 (26) .0028977 (185) -.0026962 (164) -.0026184 (48) .0021173 (53) -.0020519

The vertical excitation energy for the S_2 state is calculated to be 5.29 eV at CASSCF(10,7)/6-31G(d) level of theory. CSF 2 is estimated to have maximum contribution to this S_2 excited state of DMNA. In the following paragraphs we shall find out how to characterize this S_2 excited state inspecting CSF 2.

Excited state configurations are introduced by the following line in the excite.log file:

```
PRIMARY BASIS FUNCTION= 1 2 3 4 5 1 2 3 4 5
2 SYMMETRY TYPE = 1
1 2 3 4 5
1 2 3 4 6
3 SYMMETRY TYPE = 1
1 2 3 4 6
1 2 3 4 6
4 SYMMETRY TYPE = 1
1 2 3 4 5
1 2 3 5 6
```

(10,7) active space contains 5 doubly occupied bonding orbitals. The first line indicates that all the 5 orbitals are doubly occupied for the ground state which is denoted as 1 2 3 4 5 1 2 3 4 5 for this system. Configuration 2 is a single excitation, with one electron

moving from the 5th to 6th orbital within the active space. Configuration 3 is double excitation: both electrons from 5th orbital are promoted to the 6th orbital within the active space. CSF 2 has the maximum coefficient (0.916317) for the S₂ excited state, which means that the S₂ excited state is primarily composed of configuration 2. Configuration 2 infers excitation of an electron from 5th to 6th orbital within the active space. Inspection of nature of the 5th and 6th orbital can be done using visualization software like ChemCraft. 5th and 6th orbitals correspond to $n\sigma_o$ and π_{ONO}^* , respectively, as illustrated in Figure 3. Thus, S₂ excited state correspond to an (n,π^*) state, which infers excitation of an electron from 5th orbital ($n\sigma_o$) to 6th orbital (π_{ONO}^*) within the active space. The procedure described here gives a general idea how to characterize an excited state.

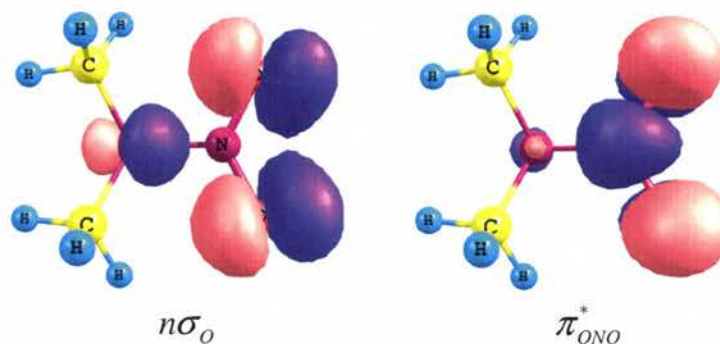


Figure 3: 5th orbital is computed to be $n\sigma_o$ and 6th orbital is computed to be π_{ONO}^* at CASSCF(10,7)/6-31G(d) level of theory for DMNA.

CASE STUDY II: Furazan: Molpro Example

Procedure of selecting active space in Molpro is different from that in Gaussian. In contrast to Gaussian, No ordering of the orbitals is needed for Molpro. In Molpro, occupied orbitals including all antibonding orbitals incorporated in the active space and

all the bonding orbitals are specified with the *Occ* keyword. Then, the number of bonding orbitals which are not in active space are specified with the *Closed* keyword. Thus, *Occ*–*Closed* indicates number of active orbitals.

The above idea is exemplified for furazan molecule. Furazan molecule has total 36 electrons, that reside in 18 doubly occupied bonding molecular orbitals. If (10,7) active space is selected according to Gaussian notation, 5 bonding orbitals and 2 antibonding orbitals need to be included in the active space for this molecule. According to Molpro notation, the same active space is defined by Occ,20; Closed,13, which means $(20-13)=7$ orbitals are in the active space and $(18-13)\times 2=10$ electrons will be distributed in 7 active orbitals.

Here is the input file for the CASSCF calculation:

{taken from the excite1.com file}

```
memory,500,m
basis=STO-3G
geomtyp=xyz
geometry={
7
furazan
C,-0.883100000,-0.014698000,-6.001659000
C,-0.883100000,1.114352000,-5.166470000
N,-0.883101000,0.720111000,-3.896518000
O,-0.883100000,-0.652240000,-3.957517000
N,-0.883101000,-1.112658000,-5.252240000
H,-0.883100000,-0.092968000,-7.079404000
H,-0.883100000,2.167441000,-5.407742000
}
gprint,basis;
gprint,orbital;
rhf
orbital,2100.2,Printorb,1000;
CASSCF:Occ,20;Closed,13;
wf,36,0;
start,2100.2;
orbital,2140.2,Print,1000;
natorb,CI,Print;
natorb,2001.2,Print=1000;
```

At the output file the CASSCF energy is printed to be -257.32398664 Hartree. This energy corresponds to the ground state energy of this molecule at CASSCF(10,7)/STO-3G level of theory. To compute excited state energy, another line is included in the input file: State, n1,n2,n3; n1 corresponds to the number of states, n2 correspond to the number of states to be included to perform state average calculation, n3 corresponds to the root.

Here is an input file to calculate S₁ excited state of furazan:

```
memory,500,m
basis=STO-3G
geomtyp=xyz
geometry={
7
furazan
C, -0.883100000, -0.014698000, -6.001659000
C, -0.883100000, 1.114352000, -5.166470000
N, -0.883101000, 0.720111000, -3.896518000
O, -0.883100000, -0.652240000, -3.957517000
N, -0.883101000, -1.112658000, -5.252240000
H, -0.883100000, -0.092968000, -7.079404000
H, -0.883100000, 2.167441000, -5.407742000
}
gprint,basis;
gprint,orbital;
rhf
CASSCF;Occ,20;Closed,13;
wf,36, .0;State,2,1,2;
start,2100.2;
orbital,2140.2,Print,1000;
natorb,CI,Print;
natorb,2001.2,Print=1000;
```

Here the keyword *State,2,1,2* is specified to compute the S₁ excited state energy, which is computed to be 6 eV. The routine described above can be used to compute the excited state energy of any compounds using Molpro.

References:

1. Roos, B. O. *Adv. Chem. Phys.* **1987**, 69, 399.
2. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J.; Vreven, J. A. T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara,

- M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *GAUSSIAN 03, (Revision B.04)*, Gaussian, Inc., Pittsburgh, PA, **2003**.
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 4. Bhattacharya, A.; Guo, Y. Q.; Bernstein, E. R. *J. Phys. Chem. A* **2009**, *113*, 811.
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APPENDIX V

The Nonadiabatic Chemistry through Conical Intersections

Introduction

The adiabatic Born-Oppenheimer approximation (BOA),¹ which separates electronic and nuclear motions of a molecule, is the keystone to the visualization of chemical processes. This approximation enables us to picture molecules as a set of nuclei moving over a potential energy surface created by the faster moving electrons. Despite its central role in chemical theory, breakdown of the adiabatic BOA is particularly common in the photochemistry and photophysics of polyatomic molecules,² for which a large number of energetically close-lying electronic states and many degrees of freedom exist. Specific examples of the breakdown of the adiabatic BOA include charge transfer,³ electronic quenching, and spin forbidden reactions⁴ and nature's two most basic processes: the initial radiationless energy transport step in photosynthesis⁵ and the cis-trans isomerization⁶ that initiates the process of vision.

The breakdown of BOA leads to the formation of a conical intersection between electronic potential energy surfaces.² A conical intersection is a point/seam at which two adiabatic potential energy surfaces cross. While an infinite variety of intersections are possible, conical intersections can be usually distinguished from the nuclear coordinate dependence of the potential energy surfaces near the intersection.⁷ If the

potential energy surfaces depend linearly on the nuclear coordinates near the intersection the confluence is referred to as a conical intersection since the local topology near the intersection is that of a double cone, as illustrated in Figure 1.

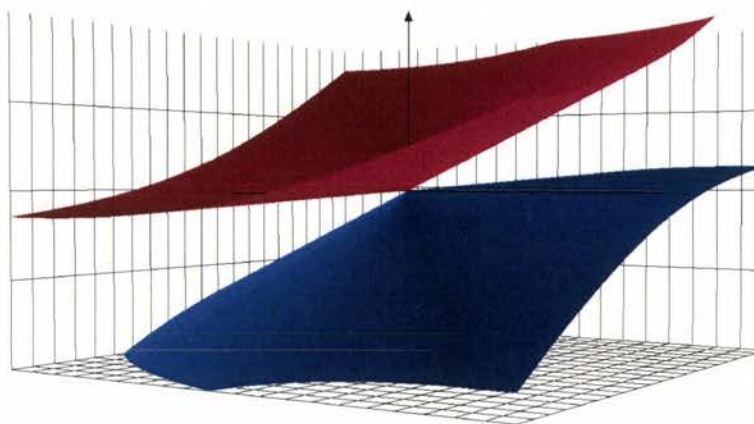


Figure 1: A generic picture of nonadiabatically coupled potential energy surfaces with a conical intersection.

Conical intersections are now firmly established to be key features in the excited electronic states processes of polyatomic molecules.^{2,8} They provide an efficient and ultrafast pathway for radiationless transition between electronic states. When a conical intersection is involved in a chemical or physical process, the nuclei move on more than one adiabatic Born-Oppenheimer potential energy surface. This process is called a nonadiabatic one and the radiationless transition between electronic states through a conical intersection is called a nonadiabatic transition. The probability for a nonadiabatic transition is high if the nuclei encounter a conical intersection at which point the two potential energy surfaces are energetically in close proximity.

In general, a number of intrinsic issues are associated with nonadiabatic chemistry through conical intersections: these concern molecular electronic structure, nuclear dynamics, and the interaction of the molecule with the radiation field. All these

issues can have significant influence on understanding and controlling excited electronic state decomposition of energetic materials.⁹ Therefore, it is an important task to summarize the essential aspects of nonadiabatic chemistry through conical intersections as they are often found to be scattered throughout the chemical physics literature. With this intension in mind, this appendix provides a concise theoretical introduction of early and present thinking of nonadiabatic chemistry involving conical intersections and their characterization using the Gaussian 03.

Theoretical Background

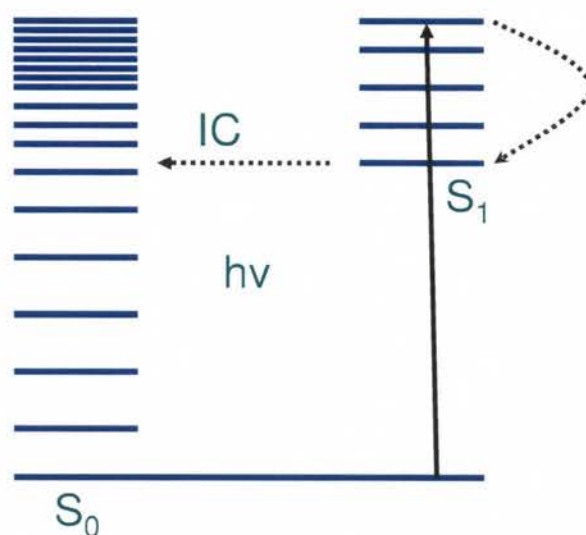


Figure 2: A schematic of the old picture of processes involving excited electronic states: Jablonski diagram. Fermi's golden rule approach is based on the vibronic states shown in the diagram.

Early thinking about nonadiabatic transitions between different electronic states was dominated by the application of Fermi's golden rule in the context of energy level diagrams,¹⁰ as illustrated in Figure 2. In this picture, the nonadiabatic transition rate is expressed as

$$k_{nt}(S_1 \rightarrow S_0) = \frac{2\pi}{\hbar} \sum |V_{if}|^2 \rho(E) \quad (1)$$

Here i and f refer to the initial and final vibrational eigen states on the S_i and S_o adiabatic Born-Oppenheimer electronic potential energy surfaces, respectively. The matrix element V_{if} represents the electronic coupling between these adiabatic Born-Oppenheimer states. Finally the density of states of S_o at the given energy E is denoted $\rho(E)$.

Fermi's golden rule is derived from perturbation theory and is valid as long as the coupling between electronic states is weak. Only detailed knowledge of the final vibrational eigen states would allow one to extract any information about product branching ratios in processes involving excited electronic states. This requires complete solution of the vibrational Schrödinger equation, which is impractical for most polyatomic molecules. Therefore, direct quantitative use of Fermi's golden rule to describe nonadiabatic processes of polyatomic molecules is practically impossible.

In order to describe the processes involving excited electronic states, a more convenient theoretical framework should go beyond the BOA. This allows nonadiabatic transitions between different electronic states by introducing the terms neglected in adiabatic BOA: they are called nonadiabatic coupling terms. Within the adiabatic representation of the electronic states, the dominant term that controls the breakdown of the BOA^{2(b)} is the nonadiabatic coupling term:

$$\left\langle \psi_f \left| \frac{\partial}{\partial R} \right| \psi_i \right\rangle = \frac{\left\langle \psi_f \left| \frac{\partial H}{\partial R} \right| \psi_i \right\rangle}{(E_i(R) - E_f(R))} \quad (2)$$

This equation highlights the singular behavior of the nonadiabatic coupling term near a conical intersection, at which the adiabatic electronic energies E_i and E_f are equal. Thus, when a CI is present, integrals over the nuclear coordinates involving

nonadiabatic coupling terms will be dominated by geometry near the CI, not by geometry near the FC point. If the geometries corresponding to these CIs are distant from the FC point, the form of the nuclear wavefunction and electronic coupling in this region will be poorly approximated by low order expansions around the FC point. This low order expansion of a PES around its FC point is often used to evaluate $|V_{if}|$ in Fermi's golden rule. Thus, even if equation (1) for Fermi's golden rule is strictly valid, the subsequent approximation used to evaluate $|V_{if}|$ becomes questionable and quantitative application of the FGR approach to unimolecular chemistry is difficult. In many polyatomic molecules of photochemical interest, the relevant CIs are indeed far away from the FC point, and the FGR approach with the usual approximations is not appropriate. Detailed nonadiabatic theory is more appropriate to describe nonadiabatic processes. In general, these electronically nonadiabatic processes are mediated by conical intersections.

Thus, to explore nonadiabatic chemistry, understanding dynamics through conical intersections is important and appropriate. Conical intersections, also called photochemical funnels, provide pathways for ultrafast internal conversion or intersystem crossing, i.e., on the femtosecond time scale. Recent publications, both experimental and theoretical,^{2,8} show that the existence and relevance of such intersections is no longer in doubt. The rich literature on photochemistry and photophysics through conical intersections teaches us a number of general phenomena which are discussed in the following section.

Electronic Excitation and Nonadiabatic Chemistry Involving Conical Intersections

Electronic excitation promotes a molecule from its ground to an excited electronic state. As illustrated in the Figure 3, the nuclei in the electronic ground state are assumed to have their positions characterized by point p' in the reaction coordinate space. Electronic excitation takes place so fast that the nuclei do not have enough time to move. Thus the positions of the nuclei in the excited electronic state are identical to those in the ground state (classical Franck-Condon rule). The quantum mechanical analogue of the classical Franck-Condon rule is that the probability of the nuclei making a transition from one potential energy surface to another is greatest for those places at which the square of the overlap between the vibrational wavefunction of the initial and final states $q_{v'v''} \equiv \langle \psi_{v'}(R) | \psi_{v''}(R) \rangle^2$, called Franck-Condon factor, is the greatest. Thus FC point in Figure 3 shows the very essence of the Franck-Condon rule – a vertical transition.

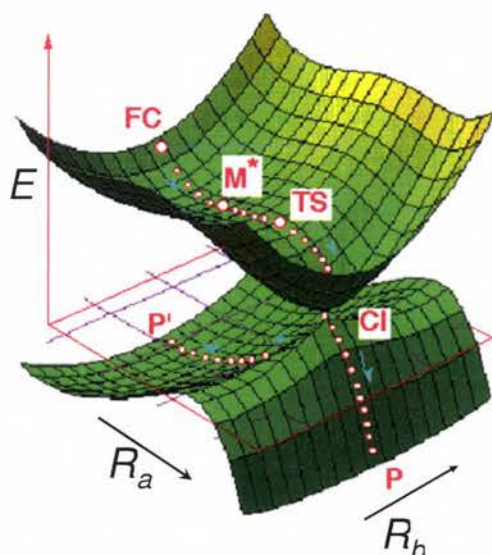


Figure 3: Generic view of nonadiabatic chemistry through a conical intersection. Conical intersection can mediate successful photochemistry by directing the molecule to the product side following nonadiabatic transition through it.^{2(c)}

The nuclear configuration at the FC point of the upper excited state may differ quite significantly from the nearest potential energy minimum M^* in the excited state PES. In a few or a few tens of femtoseconds, the system “slides down” (evolves) from P' to the neighborhood of M^* , transforming its potential energy into kinetic energy. This occurs because of the force $\left(\frac{\partial V}{\partial R}\right)$ on the nuclei due to the change in the electronic configuration from S_0 to S_1 . If M^* is separated from the conical intersection by a barrier, as soon as the molecule during vibration overcomes the barrier at TS, by going over it or by tunneling, it will be driven by the new force to the conical intersection “attractor” with almost 100% probability. At the conical intersection the molecule undergoes a nonadiabatic, nonradiative transition to the ground state through the $(S_1/S_0)_{CI}$ at the intersection of the S_1 and S_0 PESs. If the relative momentum of the nuclei is large enough, the system slides down along pathway toward p , the nearest minimum for the product. If the momentum is small, the system may go back to that P' , returning to the original molecule. The actual direction or path taken by the molecule will depend on the relative steepness of the two paths, i.e., the magnitude of the force $\left(\frac{\partial V}{\partial R}\right)$ for respective direction.

The total energy of course has to be conserved. In a condensed phase environment, the system finds a way to dissipate its energy, i.e., transfer an excess of electronic energy into its own molecular vibrational, rotational, and translational degrees of freedom or to those of the neighboring solvent molecules. Under gas phase isolated conditions, however, the excess electronic energy following a nonadiabatic transition through a conical intersection is stored in the vibrational (or rotational)

degrees of freedom on the ground electronic surface, which can often cause molecular fragmentation or rearrangement.

Geometrical structure near a conical intersection may mediate (locally) either a nonadiabatic photophysical processes (purely internal conversion retaining the original molecular structure) or a nonadiabatic photochemical process (leading to successful photochemistry and product formation). Extensive work done in the last decade^{2,8} points out that the fate of a nonadiabatic photochemical reaction depends not only on the conical intersection, but also on the local surface topology near the conical intersection, as illustrated in Figure 4. Three basic types of photochemical reaction pathways are found in organic chromophores.^{2(c)} Path (a) corresponds to that of a successful photochemical reaction, for which a finite percentage of the absorbed photon energy is used to produce a different chemical species. Path (b) shows the production of a ground state short lived new chemical species, but this species is immediately converted to the original material and no net chemical reaction is accomplished. Path (c) illustrates an aborted photochemical reaction at or near conical intersection.

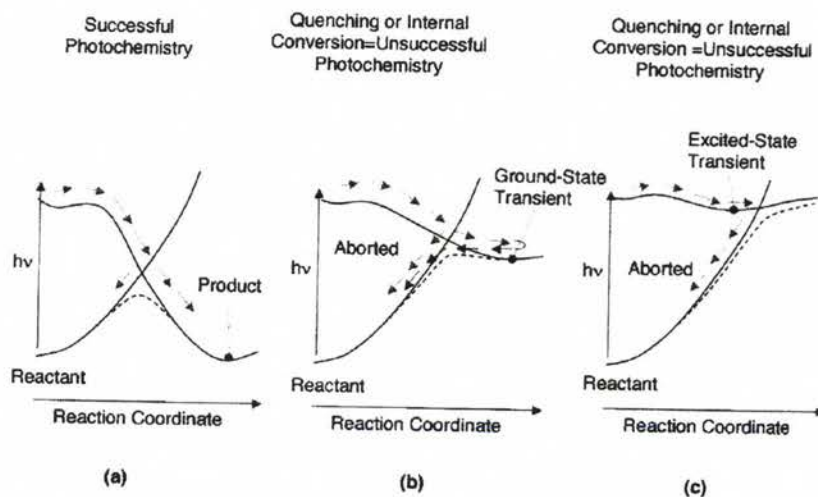


Figure 4: Three basic types of photochemical nonadiabatic reaction path involving conical intersection.^{2(c)}

Characterization of the Conical Intersection

In thermal organic reactions, molecular structure associated with the transition state often provides information on the expected products. Similarly, in a photochemical reaction, geometry associated with a conical intersection is often found to be related to the expected photoproducts. Therefore, characterization of chemically relevant low lying conical intersections of energetic materials serves as an important component in the development of theoretical understanding of excited electronic state decomposition of these materials. This can be accomplished using Gaussian 03 with *Opt = Conical* option.¹¹ Among different practical algorithms, the Gaussian program uses a projected gradient technique to characterize lowest lying conical intersections.¹²

For polyatomic molecules, two adiabatic states, even with the same symmetry, may intersect and form a conical intersection. Only for diatomic molecules, where there is only one degree of freedom, electronic states with same symmetry do not cross, yielding a non-crossing rule.¹³ At a conical intersection, one can distinguish two directions, *g* and *h*¹² such that if one were to plot the energy in the subspace of these two geometric variables (combination of bond lengths, angles, etc.) the potential energy would have the form of a double cone in the region of the degeneracy, shown in the Figure 5(a). Thus the *g-h* internal coordinates lifts the degeneracy linearly near conical intersection.

In the remaining $N-2$ (where N is number of degrees of freedom) directions, the energies of the ground and the excited electronic states may remain equal producing a seam, as shown in Figure 5(b). The lowest energy point on the seam, called lowest energy conical intersection, can be optimized and localized using a projected gradient

algorithm, as implemented in Gaussian 03. In this search, the energy of the excited state is minimized. At the same time, the energy difference between the excited state and the closest lower energy state is minimized. The condition chosen for the minimization of $(E_2 - E_1)$ in the g-h plane is¹²

$$\frac{\partial}{\partial q}(E_2 - E_1)^2 = 2(E_2 - E_1) \frac{\partial}{\partial q}(E_2 - E_1) = 0. \quad (3)$$

Here $\frac{\partial}{\partial q}(E_2 - E_1)$ is called gradient difference vector. Because, $(E_2 - E_1)^2$ varies more smoothly than $(E_2 - E_1)$ in the vicinity of the conical intersection, this approach is suitable for the minimization process. Gaussian software constructs the g-h plane from CASSCF wavefunction. The lowest energy conical intersection optimization can be performed by this software using *opt = conical* option.

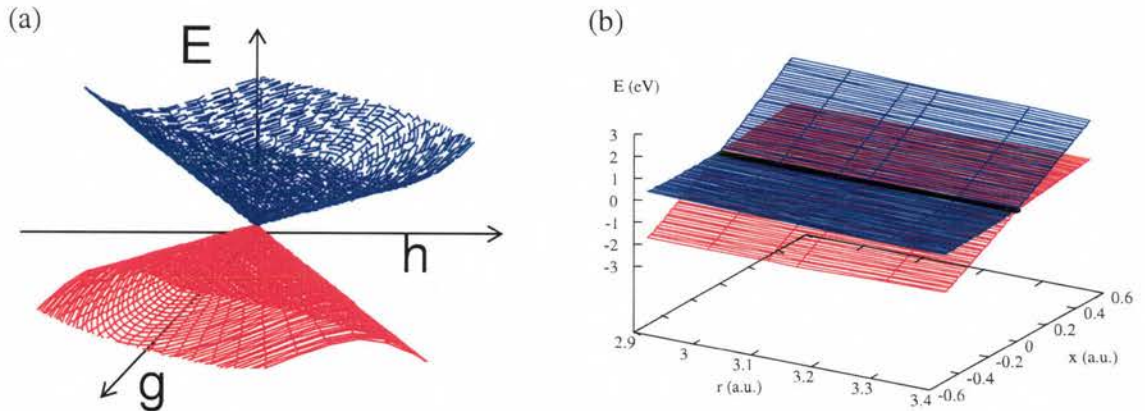


Figure 5: (a) Two internal coordinates lifts the degeneracy linearly: g-h or branching plane. (b) N-2 coordinates form the seam: points of conical intersections are connected continuously.

References

1. Born, M.; Oppenheimer, J. R. *Ann. Phys. (Leipzig)* **1927**, 84, 457.

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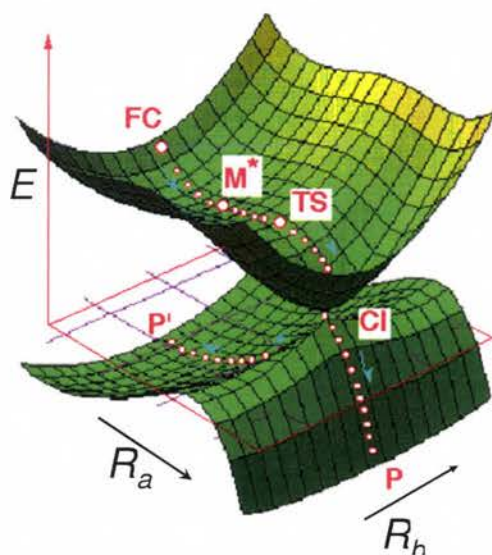


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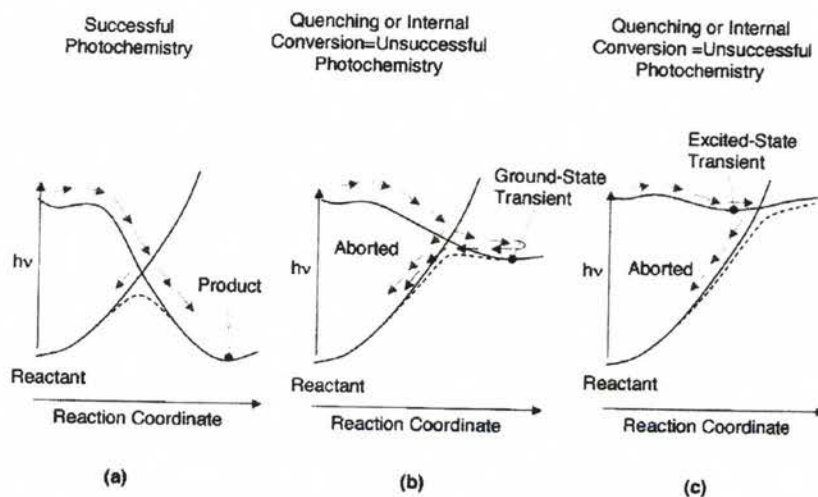


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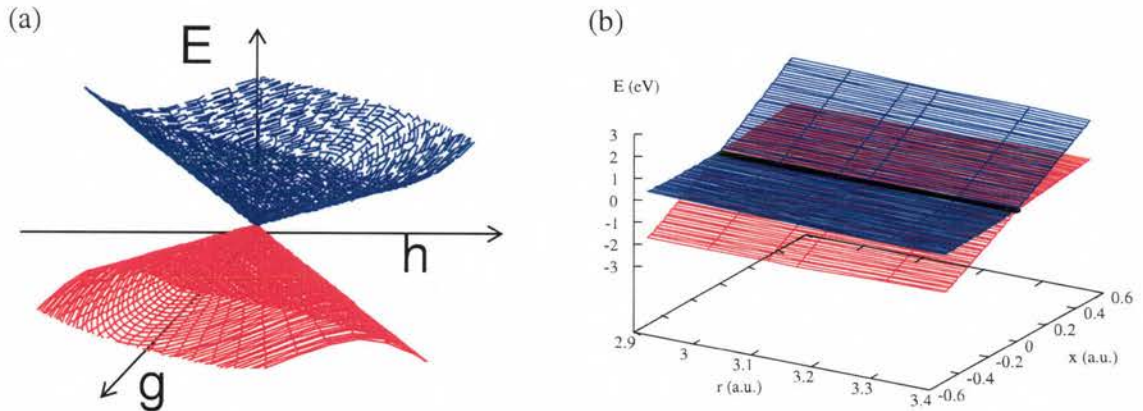


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1. Born, M.; Oppenheimer, J. R. *Ann. Phys. (Leipzig)* **1927**, 84, 457.

nonadiabatic coupling terms will be dominated by geometry near the CI, not by geometry near the FC point. If the geometries corresponding to these CIs are distant from the FC point, the form of the nuclear wavefunction and electronic coupling in this region will be poorly approximated by low order expansions around the FC point. This low order expansion of a PES around its FC point is often used to evaluate $|V_{if}|$ in Fermi's golden rule. Thus, even if equation (1) for Fermi's golden rule is strictly valid, the subsequent approximation used to evaluate $|V_{if}|$ becomes questionable and quantitative application of the FGR approach to unimolecular chemistry is difficult. In many polyatomic molecules of photochemical interest, the relevant CIs are indeed far away from the FC point, and the FGR approach with the usual approximations is not appropriate. Detailed nonadiabatic theory is more appropriate to describe nonadiabatic processes. In general, these electronically nonadiabatic processes are mediated by conical intersections.

Thus, to explore nonadiabatic chemistry, understanding dynamics through conical intersections is important and appropriate. Conical intersections, also called photochemical funnels, provide pathways for ultrafast internal conversion or intersystem crossing, i.e., on the femtosecond time scale. Recent publications, both experimental and theoretical,^{2,8} show that the existence and relevance of such intersections is no longer in doubt. The rich literature on photochemistry and photophysics through conical intersections teaches us a number of general phenomena which are discussed in the following section.

Electronic Excitation and Nonadiabatic Chemistry Involving Conical Intersections

Electronic excitation promotes a molecule from its ground to an excited electronic state. As illustrated in the Figure 3, the nuclei in the electronic ground state are assumed to have their positions characterized by point p' in the reaction coordinate space. Electronic excitation takes place so fast that the nuclei do not have enough time to move. Thus the positions of the nuclei in the excited electronic state are identical to those in the ground state (classical Franck-Condon rule). The quantum mechanical analogue of the classical Franck-Condon rule is that the probability of the nuclei making a transition from one potential energy surface to another is greatest for those places at which the square of the overlap between the vibrational wavefunction of the initial and final states $q_{v'v''} \equiv \langle \psi_{v'}(R) | \psi_{v''}(R) \rangle^2$, called Franck-Condon factor, is the greatest. Thus FC point in Figure 3 shows the very essence of the Franck-Condon rule – a vertical transition.

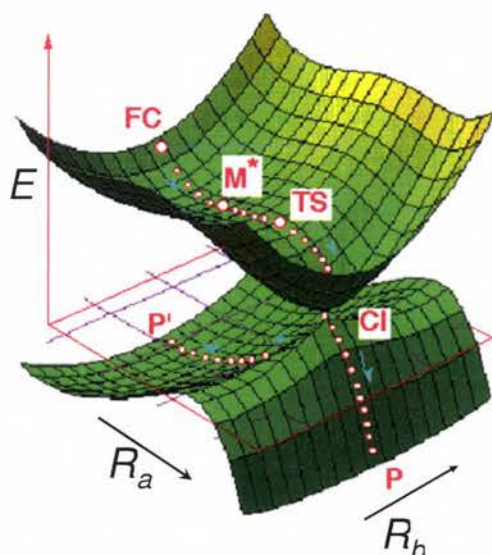


Figure 3: Generic view of nonadiabatic chemistry through a conical intersection. Conical intersection can mediate successful photochemistry by directing the molecule to the product side following nonadiabatic transition through it.^{2(c)}

The nuclear configuration at the FC point of the upper excited state may differ quite significantly from the nearest potential energy minimum M^* in the excited state PES. In a few or a few tens of femtoseconds, the system “slides down” (evolves) from P' to the neighborhood of M^* , transforming its potential energy into kinetic energy. This occurs because of the force $\left(\frac{\partial V}{\partial R}\right)$ on the nuclei due to the change in the electronic configuration from S_0 to S_1 . If M^* is separated from the conical intersection by a barrier, as soon as the molecule during vibration overcomes the barrier at TS, by going over it or by tunneling, it will be driven by the new force to the conical intersection “attractor” with almost 100% probability. At the conical intersection the molecule undergoes a nonadiabatic, nonradiative transition to the ground state through the $(S_1/S_0)_{CI}$ at the intersection of the S_1 and S_0 PESs. If the relative momentum of the nuclei is large enough, the system slides down along pathway toward p , the nearest minimum for the product. If the momentum is small, the system may go back to that P' , returning to the original molecule. The actual direction or path taken by the molecule will depend on the relative steepness of the two paths, i.e., the magnitude of the force $\left(\frac{\partial V}{\partial R}\right)$ for respective direction.

The total energy of course has to be conserved. In a condensed phase environment, the system finds a way to dissipate its energy, i.e., transfer an excess of electronic energy into its own molecular vibrational, rotational, and translational degrees of freedom or to those of the neighboring solvent molecules. Under gas phase isolated conditions, however, the excess electronic energy following a nonadiabatic transition through a conical intersection is stored in the vibrational (or rotational)

degrees of freedom on the ground electronic surface, which can often cause molecular fragmentation or rearrangement.

Geometrical structure near a conical intersection may mediate (locally) either a nonadiabatic photophysical processes (purely internal conversion retaining the original molecular structure) or a nonadiabatic photochemical process (leading to successful photochemistry and product formation). Extensive work done in the last decade^{2,8} points out that the fate of a nonadiabatic photochemical reaction depends not only on the conical intersection, but also on the local surface topology near the conical intersection, as illustrated in Figure 4. Three basic types of photochemical reaction pathways are found in organic chromophores.^{2(c)} Path (a) corresponds to that of a successful photochemical reaction, for which a finite percentage of the absorbed photon energy is used to produce a different chemical species. Path (b) shows the production of a ground state short lived new chemical species, but this species is immediately converted to the original material and no net chemical reaction is accomplished. Path (c) illustrates an aborted photochemical reaction at or near conical intersection.

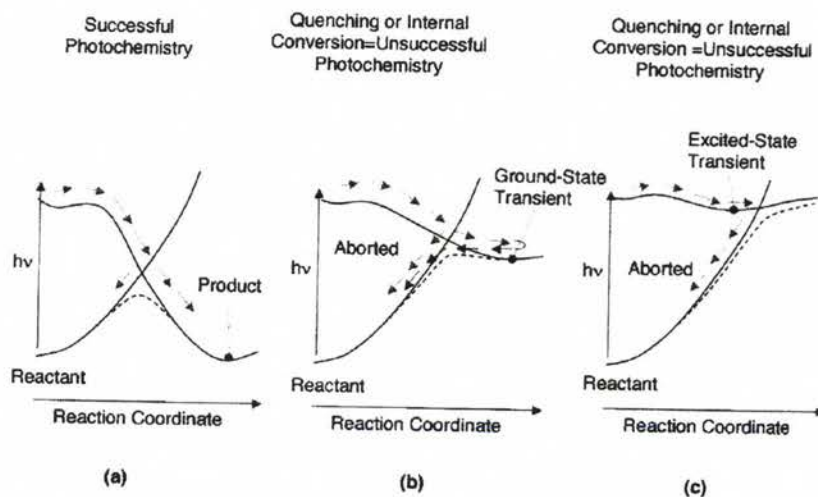


Figure 4: Three basic types of photochemical nonadiabatic reaction path involving conical intersection.^{2(c)}

Characterization of the Conical Intersection

In thermal organic reactions, molecular structure associated with the transition state often provides information on the expected products. Similarly, in a photochemical reaction, geometry associated with a conical intersection is often found to be related to the expected photoproducts. Therefore, characterization of chemically relevant low lying conical intersections of energetic materials serves as an important component in the development of theoretical understanding of excited electronic state decomposition of these materials. This can be accomplished using Gaussian 03 with *Opt = Conical* option.¹¹ Among different practical algorithms, the Gaussian program uses a projected gradient technique to characterize lowest lying conical intersections.¹²

For polyatomic molecules, two adiabatic states, even with the same symmetry, may intersect and form a conical intersection. Only for diatomic molecules, where there is only one degree of freedom, electronic states with same symmetry do not cross, yielding a non-crossing rule.¹³ At a conical intersection, one can distinguish two directions, *g* and *h*¹² such that if one were to plot the energy in the subspace of these two geometric variables (combination of bond lengths, angles, etc.) the potential energy would have the form of a double cone in the region of the degeneracy, shown in the Figure 5(a). Thus the *g-h* internal coordinates lifts the degeneracy linearly near conical intersection.

In the remaining $N-2$ (where N is number of degrees of freedom) directions, the energies of the ground and the excited electronic states may remain equal producing a seam, as shown in Figure 5(b). The lowest energy point on the seam, called lowest energy conical intersection, can be optimized and localized using a projected gradient

algorithm, as implemented in Gaussian 03. In this search, the energy of the excited state is minimized. At the same time, the energy difference between the excited state and the closest lower energy state is minimized. The condition chosen for the minimization of $(E_2 - E_1)$ in the g-h plane is¹²

$$\frac{\partial}{\partial q}(E_2 - E_1)^2 = 2(E_2 - E_1) \frac{\partial}{\partial q}(E_2 - E_1) = 0. \quad (3)$$

Here $\frac{\partial}{\partial q}(E_2 - E_1)$ is called gradient difference vector. Because, $(E_2 - E_1)^2$ varies more smoothly than $(E_2 - E_1)$ in the vicinity of the conical intersection, this approach is suitable for the minimization process. Gaussian software constructs the g-h plane from CASSCF wavefunction. The lowest energy conical intersection optimization can be performed by this software using *opt = conical* option.

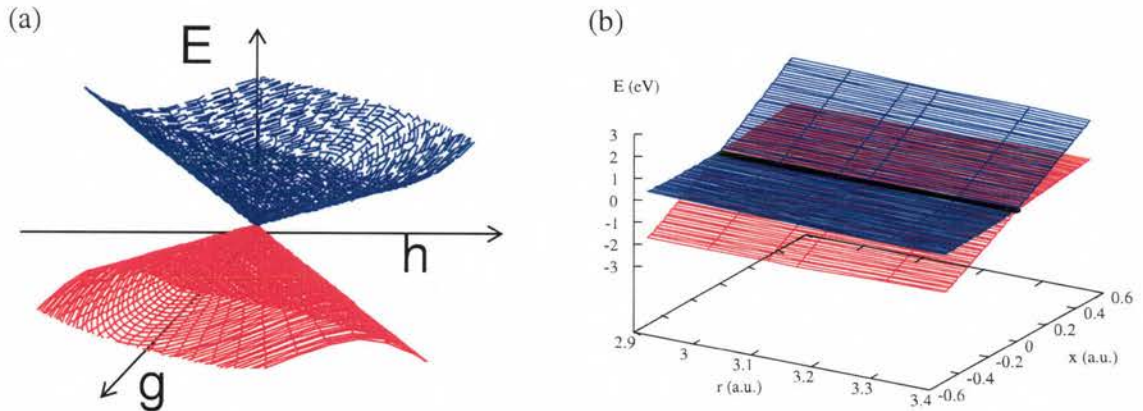


Figure 5: (a) Two internal coordinates lifts the degeneracy linearly: g-h or branching plane. (b) N-2 coordinates form the seam: points of conical intersections are connected continuously.

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Supplementary Information

Derivation and Analysis of the Nuclear Schrödinger Equation:^{2(a)}

The molecular Hamiltonian, $\hat{H}$, can be written

$$\hat{H}(R, r) = \hat{T}_n(R) + \hat{T}_e(r) + \hat{U}(R, r) \quad (a)$$

where $\hat{T}_n$, $\hat{T}_e$ are the kinetic energy operator for the nuclei and electrons, respectively, and $\hat{U}$ is the potential energy function. The clamped-nucleus Hamiltonian is obtained by setting the nuclear kinetic energy to zero,

$$\hat{H}_{cl}(R; r) = \hat{T}_e(r) + \hat{U}(R; r) \quad (b)$$

For any value of the parameter R , its eigenvalues, V , and eigenfunctions Φ , can be found from

$$\hat{H}_{cl}\Phi_i(R; r) = V_i(R)\Phi_i(R; r) \quad (c)$$

The set of eigenfunction are complete and orthonormal. Now total wavefunction can be expanded as follows

$$\Psi(R, r) = \sum_i \chi_i(R)\Phi_i(R; r) \quad (d)$$

where the χ_i are the nuclear function that act as the expansion coefficients. This is known as Born representation.

Now we insert equation (d) to Schrödinger equation, $i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi$, multiply from the left by one electronic function Φ_j , and integrate over the electronic coordinates. This leads to the following equation:

$$\left[\hat{T}_n + V_j \right] \chi_j - \sum_i \hat{\Lambda}_{ji} \chi_i = i\hbar \frac{\partial \chi_j}{\partial t} \quad (e)$$

where $\hat{\Lambda}_{ji} = \delta_{ji} \hat{T}_n - \langle \Phi_j | \hat{T}_n | \Phi_i \rangle$ is the nonadiabatic coupling operator. This nonadiabatic coupling operator depends inversely on the mass of the system and on the derivative coupling vector,

$$F_{ij} = \frac{\langle \Phi_i | (\Delta \hat{H}_{cl}) | \Phi_j \rangle_{i \neq j}}{V_j - V_i}$$

This derivative coupling vector F_{ij} is expressed as

$$\left\langle \psi_f \left| \frac{\partial}{\partial R} \right| \psi_i \right\rangle = \left\langle \psi_f \left| \frac{\partial H}{\partial R} \right| \psi_i \right\rangle / (E_i(R) - E_f(R)) \text{ in the appendix text; however, their general forms are the same.}$$

APPENDIX VI

The Search for the Conical Intersection (Photochemical Funnel)

Introduction

With the seminal 1935 work on the structure of potential-energy surfaces, Eyring, Evans and Polany were able to define the exact nature of the “activated complex” or “transition state” for thermochemical reactions.¹ The molecular structure of a transition state describes the spatial arrangement of the atoms corresponding to the highest point (TS) on the potential-energy surface that has to be overcome by the reactant to form the product.

In a photochemical reaction, the reactant is an electronically excited-state molecule or a complex M^* , while the product is a ground-state species. Thus, to describe a photochemical reaction, one must first establish the nature of spatial arrangement of the atoms corresponding to the point at which M^* decays from the excited-state potential-energy surface to the ground state and initiates product formation. Loosely, this critical molecular structure plays the role of the “transition state” for a photochemical process. Extensive work in the last few decades has firmly established that conical intersections, which occur at the intersection of different electronic potential energy surfaces, constitute the photochemically relevant decay channels. Photochemistry begins for a number of compounds with electronic excitation

of a molecule to an excited electronic state, proceeds to the low-lying conical intersection, undergoes a nonadiabatic transition from the upper to the lower state, and ends at the lower/ground electronic state.²

Due to the recent availability of suitable computational methods in standard quantum chemistry packages (e.g. Gaussian 03, Molpro 2000, etc.), the computation of conical intersections for organic molecules and, to a certain extent, the computation of excited-state reaction pathways, are becoming a standard practice among computational chemists. In this context, the present appendix discusses how to locate conical intersections for the energetic materials and biomolecular ions using Gaussian 03.

Steps to be completed to locate lowest energy conical intersections:

- ❖ Predict a starting geometry for the conical intersection.

This could be a relevant transition state structure, FC geometry, another isomeric minimum, etc.

- ❖ Compute and examine the canonical orbitals at the RHF/STO-3G level in order to select the active space.

Inspection of correct MOs can be easily done using a visualization software (e.g., Chemcraft). Select an appropriate active space.

- ❖ Perform a CAS/STO-3G calculation on the ground state, using the active space selected at RHF/STO-3G level. Recheck the CAS orbitals in the active space to make sure that the chosen orbitals actually are in the active space. Run a series of CAS calculations on the ground state, using the sequence of basis sets: STO-3G, 4-31G, and 6-31G(d).

- ❖ Perform a state averaged CAS/6-31G(d) calculation for the excited state of interest (as specified by the *NRoot* option). For this state averaged CAS the weight for each state need to be specified in a separate input section.

As conical intersection is an intersection between two surfaces, a state averaged CAS is necessary because only state averaged CAS orbitals provide the best description of the specified group of states as a whole. Rule of thumb is to use equal weights (0.5 and 0.5) for the two states between which conical intersection is predicted to be present.

- ❖ Once the state averaged CAS job has completed, characterize the states and compare their energies.

Generally, it is found from experience that if the FC geometry is the starting geometry, a considerably large energy difference (~1-6 eV) between excited states is found; however, a very small energy difference (~0.1 eV) is obtained for transition state or isomeric structures.

- ❖ Locate the conical intersection by running a CAS job with *Opt = Conical* option.

To begin with, increase the number of SCF iterative cycles and reduce the convergence criteria for SCF calculations (as specified by e.g., SCF(MaxCycles = 400,Conver = 6), where the default number of SCF iterative cycles is 64 and convergence criteria is 8) to speed up the calculation and to avoid SCF convergence failure problems.

References:

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CASE STUDY I: On the Excited Electronic State Decomposition of DMNA

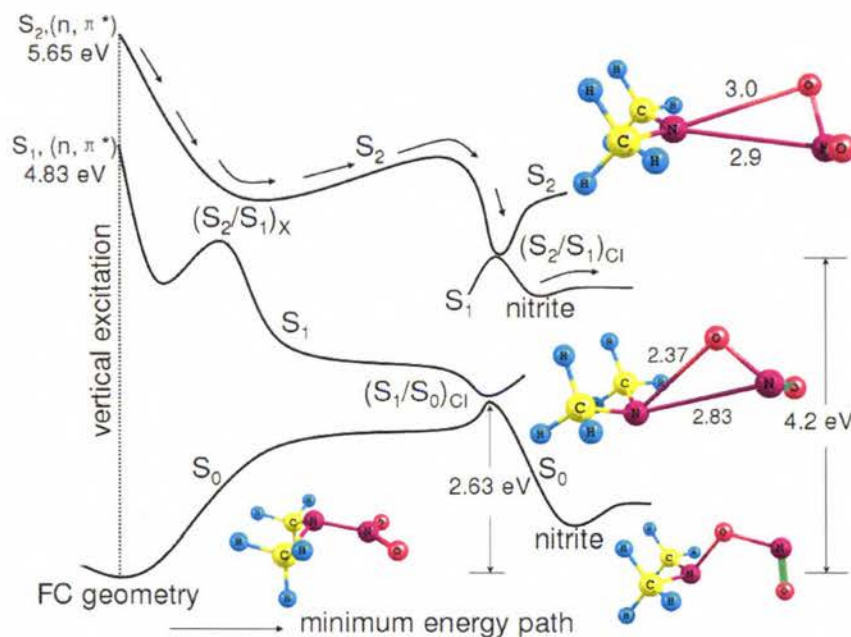
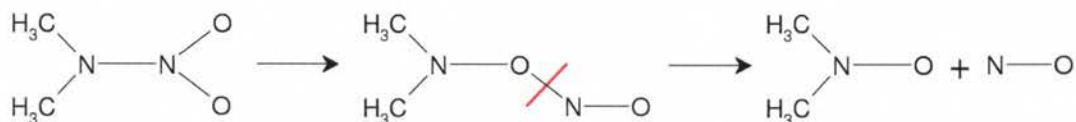


Figure 1. One dimensional projection of the multidimensional electronic potential energy surfaces of DMNA computed at the CASSCF(10,7)/6-31G(d) level of theory. Path arrows represent the classical trajectory of the plausible excited electronic state decomposition mechanism of DMNA.

DMNA undergoes a nitro-nitrite isomerization through an $(S_2/S_1)_{CI}$ conical intersection following electronic excitation to its $S_2(n,\pi^*)$ state. The reaction pathway calculated at the CASSCF(10,7)/6-31G(d) level of theory is shown in Figure 1. There are many critical points on the S_0 , S_1 , and S_2 surfaces associated with the excited state isomerization of DMNA. Here we only detail how to localize minimum energy conical intersections which are present on the reaction path of this isomerization reaction

coordinate. Once these critical points are explored one can follow the reaction path using IRC algorithm. Exploration of the reaction path following IRC algorithm is discussed in Appendix VII.

We shall start the search for conical intersections with ground state calculations for nitro-nitrite isomerization of DMNA because, transition state geometry associated with this isomerization process predicted on the ground state provides a good starting geometry for $(S_1/S_0)_{CI}$ and $(S_2/S_1)_{CI}$ conical intersections in the nitro-nitrite isomerization reaction coordinate. This prediction was made after a long search for the possible initial geometry of $(S_1/S_0)_{CI}$ and $(S_2/S_1)_{CI}$ conical intersections. Prediction of a good starting geometry is the most difficult step in the search of a conical intersection. In general, different initial starting geometries can be used: FC geometry, transition state geometry, isomerized geometry, etc. In the present case, we find that the transition state geometry associated with the nitro-nitrite isomerization process provides a good starting geometry for $(S_1/S_0)_{CI}$ and $(S_2/S_1)_{CI}$ conical intersections. The nitro-nitrite isomerization followed by extremely weak NO-NO bond scission is a thermochemically allowed decomposition mechanism of DMNA in the ground electronic state:



The nature of the transition state (TS) associated with the nitro-nitrite isomerization channel is a subject of some discussions. Both tight and loose TS geometries are reported in the literature for the nitro-nitrite isomerization in the ground state (see Chapter 2 for more detailed discussions). A tight TS geometry corresponds to

an isomerization for which rotation of NO₂ is substantial at short N-N bond length. A loose TS geometry, on the other hand, corresponds to an isomerization for which rotation of NO₂ does not happen until the N-N bond is elongated substantially.

We first need to optimize the transition state associated with nitro-nitrite isomerization on the ground state surface at the MP2/6-31G(d) level of theory. The starting geometry comes from ChemCraft. A tight geometry for nitro-nitrite isomerization TS is considered to generate the Cartesian coordinates from ChemCraft.

Optimization of nitro-nitrite isomerization TS at MP2/6-31G(d)

{taken from the opt.com file}

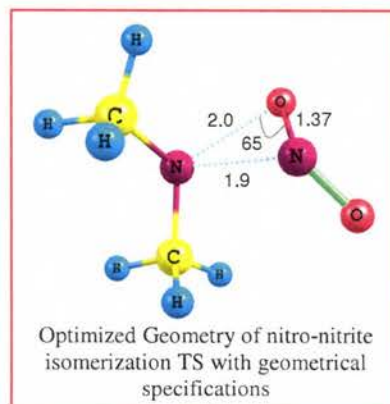
```
%chk=opt
%mem=600MB
#p MP2/6-31G(d) Opt Freq NoSymm
```

Optimization of nitro-nitrite isomerization TS

```
0      1
7      0.802668000  -0.037587000  -0.469189000
7      -0.926176000  -0.231040000   0.388917000
8      -1.805520000   0.605201000   0.390900000
8      -0.919056000  -1.121430000  -0.663563000
6      0.838018000   1.392425000  -0.257453000
6      1.590942000  -0.780726000   0.488196000
1      1.821670000   1.690395000  -0.651292000
1      0.076411000   1.876490000  -0.869919000
1      0.743450000   1.709165000   0.789073000
1      2.630457000  -0.691149000   0.139554000
1      1.304845000  -1.830737000   0.432806000
1      1.510576000  -0.414137000   1.518532000
```

This optimizes a tight nitro-nitrite isomerization TS. The fact that it is a true transition state can be verified from the imaginary frequency. Cartesian coordinate for the optimized geometry is given below:

```
7      0.802668000  -0.037587000  -0.469189000
7      -0.926176000  -0.231040000   0.388917000
8      -1.805520000   0.605201000   0.390900000
8      -0.919056000  -1.121430000  -0.663563000
6      0.838018000   1.392425000  -0.257453000
6      1.590942000  -0.780726000   0.488196000
1      1.821670000   1.690395000  -0.651292000
1      0.076411000   1.876490000  -0.869919000
1      0.743450000   1.709165000   0.789073000
1      2.630457000  -0.691149000   0.139554000
```



1	1.304845000	-1.830737000	0.432806000
1	1.510576000	-0.414137000	1.518532000

From this starting geometry we can begin the conical intersection optimization steps. First, we need initial canonical orbitals for the CASSCF computation. The orbitals we shall use are from a restricted Hartree-Fock calculation.

Preliminary examination of the orbitals

{taken from the pop.com file}

```
%chk=pop
%mem=600MB
#p RHF/STO-3G Gfinput NoSymm Pop=Full
```

Population analysis for nitro-nitrite isomerization TS geometry

0	1		
7	0.802668000	-0.037587000	-0.469189000
7	-0.926176000	-0.231040000	0.388917000
8	-1.805520000	0.605201000	0.390900000
8	-0.919056000	-1.121430000	-0.663563000
6	0.838018000	1.392425000	-0.257453000
6	1.590942000	-0.780726000	0.488196000
1	1.821670000	1.690395000	-0.651292000
1	0.076411000	1.876490000	-0.869919000
1	0.743450000	1.709165000	0.789073000
1	2.630457000	-0.691149000	0.139554000
1	1.304845000	-1.830737000	0.432806000
1	1.510576000	-0.414137000	1.518532000

We use NoSymm option because every time we run a CAS calculation on a molecule with a different symmetry Gaussian reorients the molecule for the particular point group and will destroy the active space. NoSymm disables this feature.

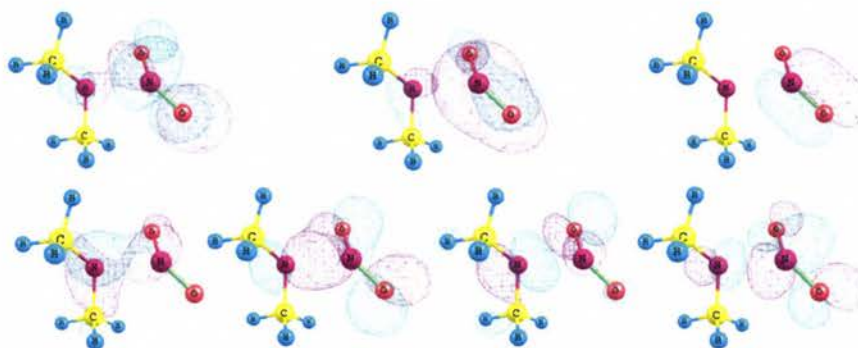


Figure 2: Active orbitals of DMNA at nitro-nitrite isomerization TS

DMNA has 48 electrons. Since we are dealing with the singlet manifold there will be 24 occupied molecular orbitals. Among 24 occupied orbitals only the highest occupied 5 orbitals and the lowest unoccupied 2 orbitals (taken from above RHF job) are selected (as illustrated in Figure 2) to construct a (10,7) active space. This (10,7) active space will be used to localize lowest energy $(S_1/S_0)_{CI}$ conical intersection of DMNA. Inspection of the correct orbitals is performed using ChemCraft.

Run a CASSCF calculation on the ground state

{taken from the opt6.com file}

```
%mem=600MB
%chk=opt6.chk
#p CASSCF(10,7,NRoot=1)/6-31G(d)
Guess=Read Pop=Full Ginput SCF=(MaxCycle=200) NoSymm
```

DMNA at nitro-nitrite isomerization TS

0	1		
7	0.802668000	-0.037587000	-0.469189000
7	-0.926176000	-0.231040000	0.388917000
8	-1.805520000	0.605201000	0.390900000
8	-0.919056000	-1.121430000	-0.663563000
6	0.838018000	1.392425000	-0.257453000
6	1.590942000	-0.780726000	0.488196000
1	1.821670000	1.690395000	-0.651292000
1	0.076411000	1.876490000	-0.869919000
1	0.743450000	1.709165000	0.789073000
1	2.630457000	-0.691149000	0.139554000
1	1.304845000	-1.830737000	0.432806000
1	1.510576000	-0.414137000	1.518532000

This optimizes CAS wave function for the ground state. Orbitals in the active space are rechecked using ChemCraft to make sure that correct orbitals are actually in the active space.

Run a CASSCF calculation for the excited state

{taken from the opt8.com file}

```
%mem=600MB
%chk=opt8.chk
#p CASSCF(10,7,NRoot=2,StateAverage)/6-31G*
Guess=Read Pop=Full Ginput SCF=(MaxCycle=200) NoSymm
```

Excitation of DMNA at nitro-nitrite isomerization TS geometry


```

0      1
7      0.802668000 -0.037587000 -0.469189000
7      -0.926176000 -0.231040000  0.388917000
8      -1.805520000  0.605201000  0.390900000
8      -0.919056000 -1.121430000 -0.663563000
6      0.838018000  1.392425000 -0.257453000
6      1.590942000 -0.780726000  0.488196000
1      1.821670000  1.690395000 -0.651292000
1      0.076411000  1.876490000 -0.869919000
1      0.743450000  1.709165000  0.789073000
1      2.630457000 -0.691149000  0.139554000
1      1.304845000 -1.830737000  0.432806000
1      1.510576000 -0.414137000  1.518532000

```

0.5000000 0.5000000

This optimizes the wave function for S_1 state giving equal weight for S_1 and S_0 states.

Optimization of $(S_1/S_0)_{CI}$ in the nitro-nitrite isomerization pathway

{taken from the opt9.com file}

```

%mem=600MB
%chk=opt9.chk
#p CASSCF(10,7,NRoot=2)/6-31G*
Guess=Read Pop=Full Gfinput SCF=(MaxCycle=400) NoSymm Opt=(Conical)

```

$(S_1/S_0)_{CI}$ of DMNA in nitro-nitrite isomerization pathway

```

0      1
7      0.798343000  0.247242000 -0.426628000
7      -2.002482000 -0.078609000 -0.160900000
8      -2.207361000 -1.218818000 -0.432507000
8      -1.176426000  0.043516000  0.876918000
6      1.249567000  1.557774000 -0.023794000
6      1.560210000 -0.812959000  0.189653000
1      2.233055000  1.741765000 -0.453226000
1      0.569120000  2.312008000 -0.396528000
1      1.332649000  1.654939000  1.055872000
1      2.548395000 -0.845063000 -0.266161000
1      1.074422000 -1.763770000  0.013934000
1      1.688795000 -0.671155000  1.259930000

```

Thus the above procedure optimizes $(S_1/S_0)_{CI}$. Convergence of the conical intersection optimization steps is confirmed by the following line in opt9.log file:

```

Item          Value      Threshold  Converged?
Maximum Force  .000065      .000450    YES
RMS Force      .000014      .000300    YES
Maximum Displacement .001404      .001800    YES
RMS Displacement .000535      .001200    YES
Predicted change in Energy=-4.222551E-08
Optimization completed.
-- Stationary point found.

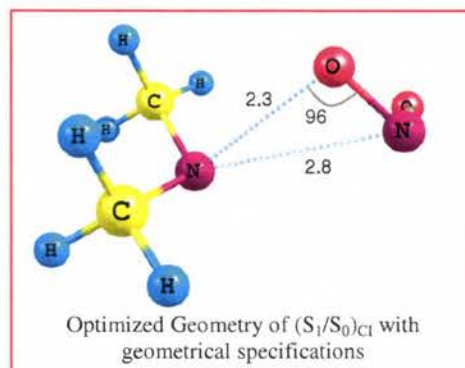
```

Cartesian coordinate of the optimized geometry for the $(S_1/S_0)_{CI}$ intersection is following:

```

7  0.798343000  0.247242000 -0.426628000
7  -2.002482000 -0.078609000 -0.160900000
8  -2.207361000 -1.218818000 -0.432507000
8  -1.176426000  0.043516000  0.876918000
6  1.249567000  1.557774000 -0.023794000
6  1.560210000 -0.812959000  0.189653000
1  2.233055000  1.741765000 -0.453226000
1  0.569120000  2.312008000 -0.396528000
1  1.332649000  1.654939000  1.055872000
1  2.548395000 -0.845063000 -0.266161000
1  1.074422000 -1.763770000  0.013934000
1  1.688795000 -0.671155000  1.259930000

```



Adiabatic energy difference between S_1 and S_0 states at the optimized geometry of $(S_1/S_0)_{CI}$ conical intersection is found to be 11 cm^{-1} . This difference can easily be calculated directly from the eigen value difference $[-337.6732412051 - (-337.6731903861)]$ between two states, obtained from the following lines in the opt9.log file.

EIGENVALUES AND EIGENVECTORS OF CI MATRIX

```

(1) EIGENVALUE      -337.6732412051
    (2) .8019048 (1) .3250542 (23) .2830195 (31) -.2608379 (89) -.1674553 (76)
    -.1418419 (114) .0974779 (69) -.0764654 (73) .0704924 (56) -.0618630 (145)
    -.0615393 (58) -.0593127 (153) .0583602 (168) -.0464649 (9) .0368153
    (192) .0356142 (88) .0325608 (45) -.0310403 (28) -.0307221 (38) -.0300519
    (8) .0279255 (112) -.0275642 (64) .0250763 (93) .0247242 (160) -.0244634
    (108) .0243465 (40) -.0242359 (182) .0241549 (173) -.0224999 (46) .0223637
    (33) -.0220090 (146) .0213722 (54) -.0189525 (11) -.0168833 (90) .0167342
    (80) -.0151920 (98) .0142379 (20) -.0128856 (78) .0124404 (29) -.0121436
    (91) -.0110141 (128) .0109551 (122) -.0108441 (121) .0108268 (35) -
    .0104925 (140) -.0103119 (177) .0100589 (24) -.0098706 (169) .0098559 (127)
    -.0096428
(2) EIGENVALUE      -337.6731903861
    (1) .5834977 (23) .5222768 (2) -.4403816 (89) -.3058082 (31) .1400915
    (73) .1251717 (56) -.1101928 (153) .1076438 (76) .0773601 (192) .0646806
    (88) .0577401 (114) -.0542332 (69) .0517213 (8) .0516870 (40) -.0473224
    (93) .0446682 (173) -.0426744 (58) .0403037 (145) .0346301 (54) -.0334363
    (168) .0247189 (29) -.0224437 (28) .0220989 (121) .0203855 (9) -.0200254
    (91) -.0196509 (38) .0189780 (177) .0185474 (127) -.0183658 (45) .0169347
    (7) .0164935 (160) .0161932 (36) -.0151619 (112) .0151213 (64) -.0141381
    (182) -.0133625 (21) -.0132431 (33) .0128629 (181) .0120554 (108) -.0117972
    (146) -.0113932 (90) -.0109835 (72) -.0108107 (196) .0106156 (59) -.0104700
    (136) -.0103757 (105) .0101490 (98) -.0095720 (46) -.0092147 (78) -
    .0087656

```

Optimization of $(S_2/S_1)_X$ Near the FC Point

Often a conical intersection between upper and lower excited electronic states is found to be near the FC point. In that case, a good starting geometry for the $(S_m / S_n)_{CI}$ (where $m > n$ and $n \neq 0$) conical intersection is the ground state FC geometry.

Following the aforementioned procedure, preliminary examination of the orbitals is done at the RHF/STO-3G level considering the FC geometry of DMNA. Subsequently first, a CASSCF calculation is performed using (14,11) active space (see Chapter 2 for detailed discussion about this active space of DMNA) and second, a state-averaged CASSCF calculation is performed for the $NRoot = 3$ giving equal (0.3333333) weight for three electronic states (S_0 , S_1 , and S_2).

Once the wave function for the state S_2 (as specified by the $NRoot = 3$ option) is optimized, we can run a CAS Opt=Conical job to locate $(S_2/S_1)_X$.

{taken from the opt3.com file}

```
%mem=500MB
%chk=opt3.chk
#p CASSCF(14,11,NRoot=3,noepmcsf)/6-31G(d)
Guess=Read Pop=Full Gfinput NoSymm SCF=(MaxCycles=900) Opt=(Conical,MaxCycles=500)
```

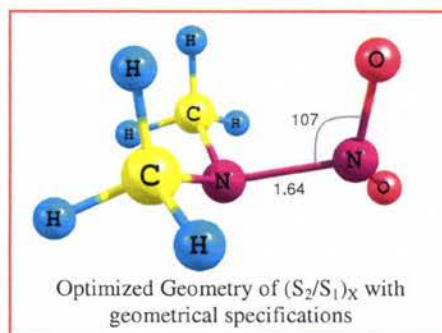
$(S_2/S_1)_X$ from the FC geometry of DMNA

0	1		
7	0.000000000	0.606152000	-0.358763000
7	-0.000001000	-0.292338000	0.786631000
8	1.091020000	-0.609441000	1.237397000
8	-1.091022000	-0.609439000	1.237398000
6	1.226870000	0.494013000	-1.131766000
6	-1.226869000	0.494012000	-1.131766000
1	1.169349000	1.230610000	-1.920793000
1	2.078358000	0.720773000	-0.512500000
1	1.357871000	-0.490712000	-1.575317000
1	-1.169348000	1.230606000	-1.920796000
1	-2.078357000	0.720774000	-0.512501000
1	-1.357871000	-0.490715000	-1.575314000

This procedure optimizes $(S_2/S_1)_X$ conical intersection. The Cartesian coordinate for the optimized geometry of the $(S_2/S_1)_X$ conical intersection is given below:

7	-0.036867000	0.769179000	-0.395974000
7	0.092161000	-0.170670000	0.951465000
8	0.511419000	-1.342280000	0.580844000

8	-0.873676000	0.163026000	1.738111000
6	1.241298000	0.641941000	-1.097476000
6	-1.187933000	0.321811000	-1.177209000
1	1.295382000	1.449725000	-1.818791000
1	2.056102000	0.761933000	-0.393029000
1	1.360550000	-0.307668000	-1.617157000
1	-1.317164000	1.041112000	-1.979892000
1	-2.076297000	0.345983000	-0.558821000
1	-1.064975000	-0.669801000	-1.610163000



Inspection of the geometry of DMNA at $(S_2/S_1)_X$ conical intersection shows that N-NO₂ bond gets elongated while the molecule evolves from the FC point of S_2 state to the $(S_2/S_1)_X$. Once different conical intersections are optimized for DMNA full reaction paths are calculated using IRC algorithm, which is a topic of discussion for Appendix VII.

CASE STUDY II: On the Ultrafast Internal Conversion of DMNA from S_1 Surface

DMNA undergoes an ultrafast (~ 50 fs) internal conversion to its ground electronic state following electronic excitation to its S_1 (n, π^*) electronic state. This ultrafast internal conversion occurs through an $(S_1/S_0)_{CI}$ conical intersection by activating an NO₂ bending mode on the S_1 excited electronic potential energy surface. A one dimensional projection of multidimensional singlet S_1 and S_0 potential energy surfaces connecting FC points to the minimum energy $(S_1/S_0)_{CI}$ conical intersection is plotted in Figure 3. This figure shows that vertical excitation of DMNA to even below the FC point of S_1 surface can potentially lead to a nonadiabatic internal conversion of electronically excited DMNA from S_1 to the S_0 surface through $(S_1/S_0)_{CI}$ conical intersection.

Often a conical intersection between upper and lower electronic states is found close to the minimum of the upper electronic surface. S_1 surface topology of DMNA

creates a similar conical intersection (as illustrated in Figure 3). In order to localize this $(S_1/S_0)_{CI}$, a geometry optimization job for DMNA on the S_1 surface is performed first using (14,11) active space. Subsequently, a state-averaged CAS *Opt = Conical* job is performed to locate $(S_1/S_0)_{CI}$ considering S_1 optimized geometry as starting geometry.

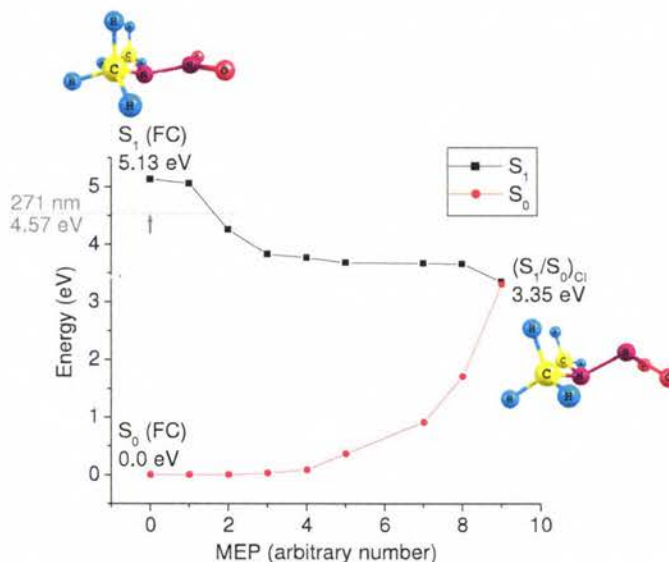


Figure 3: Minimum energy pathways from FC point to the $(S_1/S_0)_{CI}$ conical intersection following S_1 and S_0 energy gradients of DMNA, computed using IRC algorithm at CASSCF(14,11)/6-31G(d) level of theory

Optimization of DMNA on the S_1 surface

{taken from the opt4.com file}

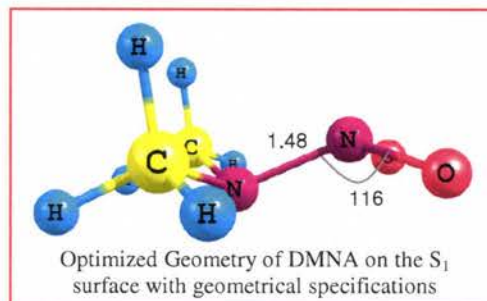
```
%mem=500MB
%chk=opt4.chk
#p CASSCF(14,11,NRoot=2)/6-31G(d)
Guess=Read Pop=Full Ginput NoSymm SCF=(MaxCycles=300) Opt
```

Opt of S_1 from FC point geometry of DMNA

```
0 1
7 0.000000000 0.606152000 -0.358763000
7 -0.000001000 -0.292338000 0.786631000
8 1.091020000 -0.609441000 1.237397000
8 -1.091022000 -0.609439000 1.237398000
6 1.226870000 0.494013000 -1.131766000
6 -1.226869000 0.494012000 -1.131766000
1 1.169349000 1.230610000 -1.920793000
1 2.078358000 0.720773000 -0.512500000
1 1.357871000 -0.490712000 -1.575317000
1 -1.169348000 1.230606000 -1.920796000
1 -2.078357000 0.720774000 -0.512501000
1 -1.357871000 -0.490715000 -1.575314000
```

This job optimizes the geometry of DMNA on the S_1 surface (as specified by the $NRoot = 2$ option). The Cartesian coordinate of the S_1 optimized geometry of DMNA is given below:

7	0.000019000	0.623204000	-0.373455000
7	0.000025000	-0.462968000	0.645546000
8	1.041693000	-0.490652000	1.455373000
8	-1.041772000	-0.490753000	1.455221000
6	1.211743000	0.486691000	-1.166757000
6	-1.211728000	0.486698000	-1.166722000
1	1.231478000	1.309857000	-1.868327000
1	2.078145000	0.566783000	-0.527068000
1	1.253891000	-0.450620000	-1.718322000
1	-1.231486000	1.309872000	-1.868283000
1	-2.078111000	0.566788000	-0.527004000
1	-1.253897000	-0.450608000	-1.718293000



This geometry is used as starting geometry to locate $(S_1/S_0)_{CI}$ conical intersection.

Optimization of $(S_2/S_1)_{CI}$ near the S_1 minimum

{taken from the opt4a.com file}

```
%mem=500MB
%chk=opt4a.chk
#p CASSCF(14,11,NRoot=2,nocpmcscf)/6-31G(d)
Guess=Read Pop=Full Ginput NoSymm
SCF=(MaxCycles=300,Conver=6) Opt(Conical,MaxCycles=600)
```

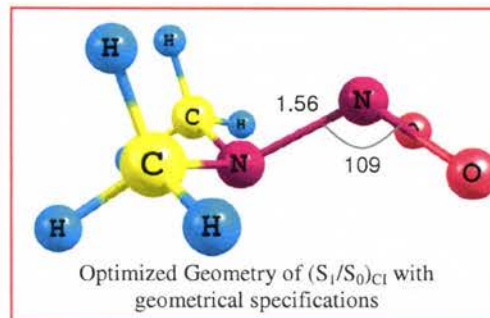
Optimization of $(S_1/S_0)_{CI}$ from S_1 minimum

0	1		
7	0.000019000	0.623204000	-0.373455000
7	0.000025000	-0.462968000	0.645546000
8	1.041693000	-0.490652000	1.455373000
8	-1.041772000	-0.490753000	1.455221000
6	1.211743000	0.486691000	-1.166757000
6	-1.211728000	0.486698000	-1.166722000
1	1.231478000	1.309857000	-1.868327000
1	2.078145000	0.566783000	-0.527068000
1	1.253891000	-0.450620000	-1.718322000
1	-1.231486000	1.309872000	-1.868283000
1	-2.078111000	0.566788000	-0.527004000
1	-1.253897000	-0.450608000	-1.718293000

This job optimizes $(S_1/S_0)_{CI}$. The Cartesian coordinate for the geometry of DMNA at

$(S_1/S_0)_{CI}$ is given below:

7	0.000179000	0.547144000	-0.425430000
7	0.000350000	-0.616829000	0.615233000
8	1.032508000	-0.385551000	1.610925000
8	-1.033328000	-0.387049000	1.609712000
6	1.233704000	0.473024000	-1.202006000
6	-1.233590000	0.473136000	-1.201686000
1	1.254377000	1.353381000	-1.828614000

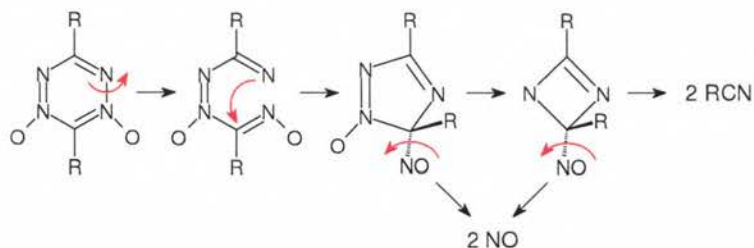


1	2.079824000	0.508863000	-0.539097000
1	1.291320000	-0.412245000	-1.825308000
1	-1.254274000	1.353392000	-1.828443000
1	-2.079502000	0.509240000	-0.538541000
1	-1.291569000	-0.412214000	-1.824836000

Inspection of the geometry of DMNA at $(S_1/S_0)_{CI}$ shows that it is quite similar to that at the minimum on the S_1 surface.

CASE STUDY III: On the Excited Electronic State Decomposition of ACTO (a tetrazine-2,4-dioxide)

ACTO undergoes ring contraction following electronic excitation, which finally leads to NO elimination. The ring contraction followed by extremely weak C-NO bond scission is a thermochemically allowed decomposition mechanism of ACTO in the ground electronic state:



Similar ring contraction mechanism can be involved in the excited electronic state decomposition of ACTO. The reaction pathway for this mechanism calculated at CASSCF(10,8)/6-31G(d) level of theory is shown in Figure 4.

We shall start with the ground state calculations for ring contracted form of ACTO because, this isomerized form predicted on the ground state provides a good starting geometry for $(S_1/S_0)_{CI}$ conical intersection in the ring contraction reaction coordinate. We first need to optimize the ring contracted form of ACTO at the RHF/6-31G(d) level of theory. The starting geometry comes from ChemCraft to generate the Cartesian coordinates for ACTO.

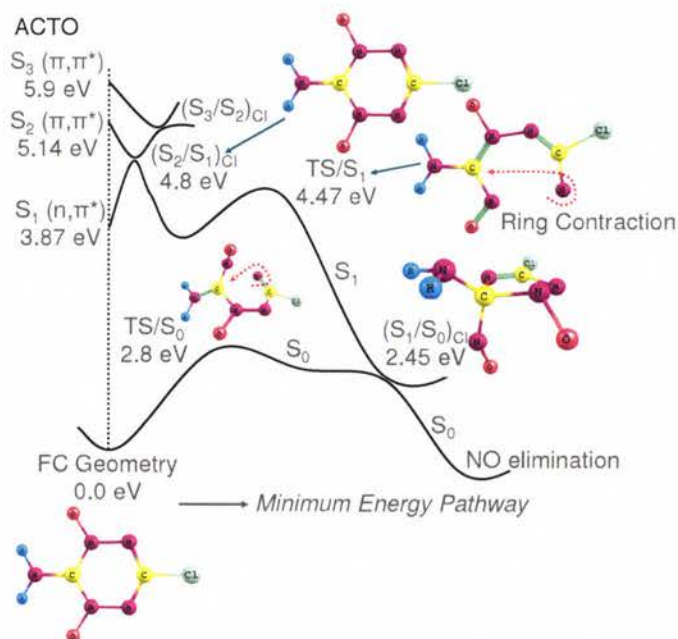


Figure 4. One dimensional projection of the multidimensional singlet electronic potential energy surfaces of ACTO computed at CASSCF(10,8)/6-31G(d) level of theory. Geometry near the $(S_1/S_0)_{Cl}$ supports a ring contraction mechanism for excited electronic state decomposition of ACTO, which finally results in NO elimination.

Optimization of ring contracted form of ACTO at RHF/6-31G(d)

{taken from the opt3.com file}

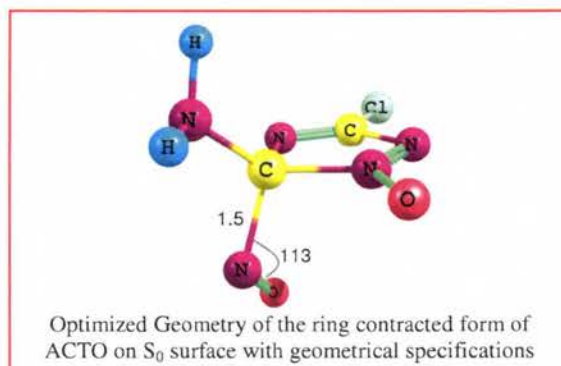
```
%chk=opt3
%mem=600MB
#p RHF/6-31G* Opt Freq NoSymm
```

ACTO opt

0	1		
6	1.137175000	0.210864000	-0.049801000
7	0.558328000	-0.618809000	-0.795737000
7	0.377243000	1.180551000	0.613427000
7	-1.602443000	-1.338676000	0.148776000
7	-0.791210000	0.911421000	0.241471000
6	-0.815289000	-0.333257000	-0.673366000
17	2.815605000	0.262539000	0.191174000
8	-1.796189000	1.483310000	0.533369000
8	-0.964464000	-1.860190000	0.970093000
7	-1.513218000	-0.164499000	-1.861662000
1	-1.049508000	0.419074000	-2.526174000
1	-2.467486000	0.100028000	-1.721128000

This job optimizes ring contracted form of ACTO. The Cartesian coordinate for the ring contracted form is given below:

6	1.137175000	0.210864000	-0.049801000
7	0.558328000	-0.618809000	-0.795737000
7	0.377243000	1.180551000	0.613427000
7	-1.602443000	-1.338676000	0.148776000
7	-0.791210000	0.911421000	0.241471000
6	-0.815289000	-0.333257000	-0.673366000
17	2.815605000	0.262539000	0.191174000
8	-1.796189000	1.483310000	0.533369000
8	-0.964464000	-1.860190000	0.970093000
7	-1.513218000	-0.164499000	-1.861662000
1	-1.049508000	0.419074000	-2.526174000
1	-2.467486000	0.100028000	-1.721128000



This geometry is used as starting geometry to locate $(S_1/S_0)_{CI}$ in the ring contraction reaction coordinate.

Preliminary examination of the orbitals

{taken from the pop.com file}

```
%chk=pop
%mem=600MB
#p RHF/STO-3G Pop=Full NoSymm Gfinput NoSymm
```

Population analysis of ACTO

0	1		
6	1.137175000	0.210864000	-0.049801000
7	0.558328000	-0.618809000	-0.795737000
7	0.377243000	1.180551000	0.613427000
7	-1.602443000	-1.338676000	0.148776000
7	-0.791210000	0.911421000	0.241471000
6	-0.815289000	-0.333257000	-0.673366000
17	2.815605000	0.262539000	0.191174000
8	-1.796189000	1.483310000	0.533369000
8	-0.964464000	-1.860190000	0.970093000
7	-1.513218000	-0.164499000	-1.861662000
1	-1.049508000	0.419074000	-2.526174000
1	-2.467486000	0.100028000	-1.721128000

5 Highest occupied molecular orbitals and 3 lowest unoccupied molecular orbitals (taken from previous RHF job) are selected (as illustrated in Figure 5) to construct a (10,8) active space. This (10,8) active space will be used to localize lowest energy

$(S_1/S_0)_{CI}$ conical intersection of DMNA. Inspection of the correct orbitals is performed using ChemCraft.

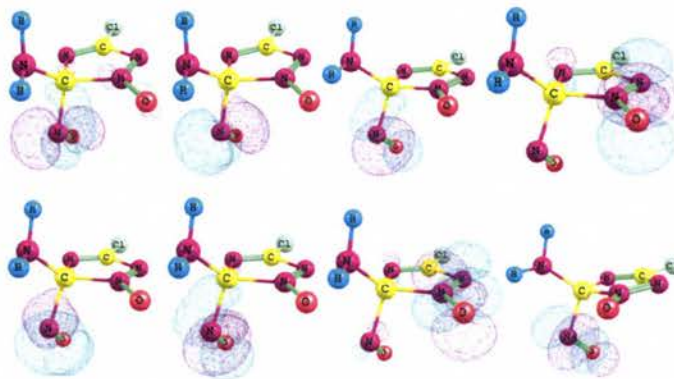


Figure 5: Active orbitals of ring contracted form of ACTO

Optimization of $(S_1/S_0)_{CI}$ in the ring contraction pathway

{taken from the ci6a.com file}

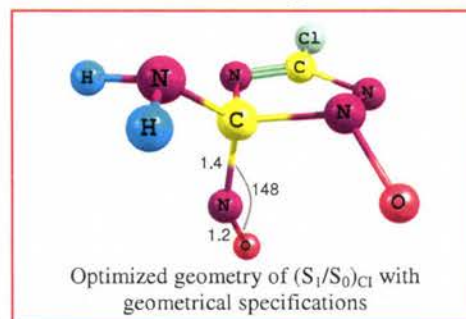
```
%chk=ci6a
%mem=600MB
#p CASSCF(10,8,NRoot=2,nocpmcscf)/6-31G* Pop=Full Ginput NoSymm Guess=read
SCF(MaxCycles=600,Conver=6) Opt(Conical,MaxCycles=600)
```

$(S_1/S_0)_{CI}$ of ACTO with (10,8) active space

0	1		
6	1.137175000	0.210864000	-0.049801000
7	0.558328000	-0.618809000	-0.795737000
7	0.377243000	1.180551000	0.613427000
7	-1.602443000	-1.338676000	0.148776000
7	-0.791210000	0.911421000	0.241471000
6	-0.815289000	-0.333257000	-0.673366000
17	2.815605000	0.262539000	0.191174000
8	-1.796189000	1.483310000	0.533369000
8	-0.964464000	-1.860190000	0.970093000
7	-1.513218000	-0.164499000	-1.861662000
1	-1.049508000	0.419074000	-2.526174000
1	-2.467486000	0.100028000	-1.721128000

This job optimizes $(S_1/S_0)_{CI}$. The Cartesian coordinate for the optimized $(S_1/S_0)_{CI}$ conical intersection is following:

6	1.195632000	0.189591000	0.025101000
7	0.580253000	-0.528150000	-0.801520000
7	0.468527000	1.140863000	0.730786000
7	-1.458559000	-1.066583000	0.090831000

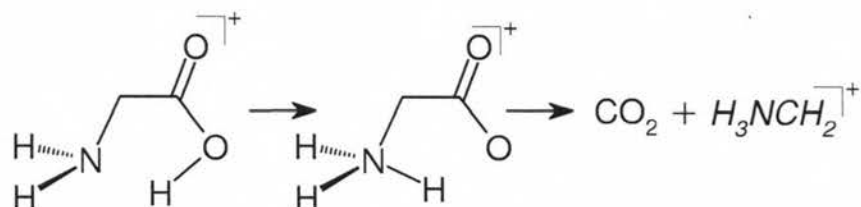


7	-0.725857000	1.153525000	-0.000899000
6	-0.806686000	-0.114316000	-0.768765000
17	2.858035000	0.034485000	0.366408000
8	-1.748438000	1.387003000	0.839456000
8	-1.508608000	-1.624526000	1.187982000
7	-1.362989000	0.065575000	-2.032218000
1	-2.311908000	0.378786000	-1.981807000
1	-1.290858000	-0.763897000	-2.584913000

The geometry at $(S_1/S_0)_{CI}$ is similar to that of ring contracted form of ACTO optimized on the ground state surface.

CASE STUDY IV: On the Conformation Specific Decomposition of Radical Cationic Glycine

Conformer II of radical cationic glycine specifically undergoes a hydrogen transfer reaction from COOH to the α -NH₂ group, followed by CO₂ elimination:



This decomposition pathway exists on both ground D_0 and excited D_1 ion state surfaces. CASSCF calculation reveals that the upper D_1 ion state surface for the conformer II of glycine is highly electronically nonadiabatically coupled to the D_0 surface along the hydrogen transfer reaction coordinate. A $(D_1/D_0)_{CI}$ conical intersection is localized in the hydrogen transfer reaction coordinate of conformer II, which is illustrated in Figure 5. This $(D_1/D_0)_{CI}$ is predicted to be involved in the decomposition of conformer II from its D_1 ion state surface. Note that here the hydrogen transfer reaction path (following procedure discussed in Appendix VII) is calculated by scanning the r_{N-H} bond distance. This calculation has missed the true conical intersection point due to the step size used

for this scan. Conical intersection, however, is optimized in a separate job using the procedure discussed below.

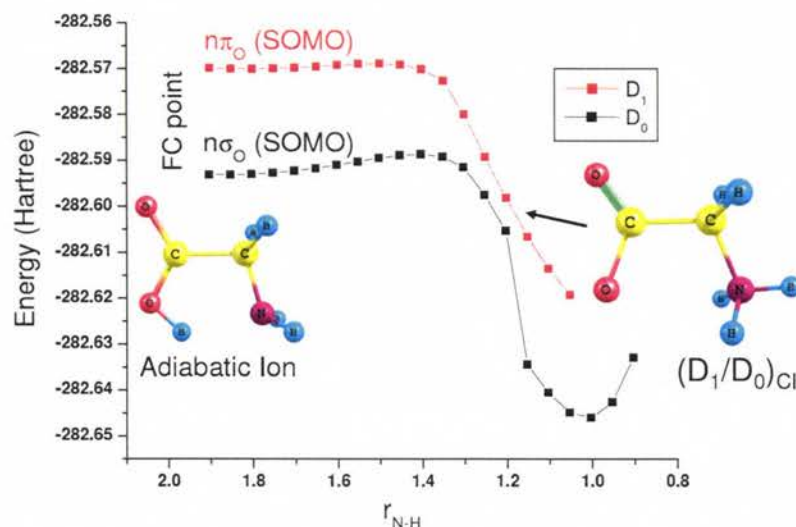


Figure 6: Hydrogen transfer pathway for conformer II of glycine with localization of $(D_1/D_0)_{CI}$.

To locate $(D_1/D_0)_{CI}$ conical intersection in the hydrogen transfer reaction coordinate we begin the CASSCF computations with the starting geometry (from UMP2 computation) of hydrogen transferred form of conformer II of glycine in the D_0 state.

Optimization of the hydrogen transferred form of conformer II of glycine

{taken from the opt.com file}

```
%chk=opt.com
%mem=600MB
#p UMP2/6-31G* Opt Freq NoSymm SCF(MaxCycles=300)
```

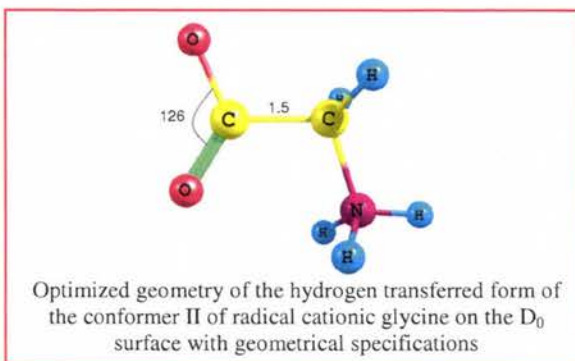
Optimization of glycine conformer II after proton transfer

1	2		
1	-0.453593000	1.904662000	1.564866000
8	-1.466659000	1.704958000	-0.713012000
8	-0.403428000	0.106924000	-1.825067000
6	-0.782337000	0.744537000	-0.744502000
6	-0.236559000	0.107751000	0.528271000
1	0.844091000	0.118711000	0.550297000
1	-0.589458000	-0.906407000	0.652177000
7	-0.752072000	0.940798000	1.656423000

1	-0.439741000	0.593368000	2.554152000
1	-1.764901000	0.966880000	1.658180000

This optimizes hydrogen transferred form of conformer II on D_0 surface. The Cartesian coordinate of the optimized geometry is as follows:

1	-0.449367000	1.919070000	1.548775000
8	-1.488111000	1.736244000	-0.702325000
8	-0.401006000	0.102535000	-1.835771000
6	-0.782927000	0.745569000	-0.742245000
6	-0.228938000	0.097183000	0.529776000
1	0.862906000	0.109212000	0.554423000
1	-0.586219000	-0.926990000	0.657419000
7	-0.751483000	0.939868000	1.655469000
1	-0.438148000	0.593206000	2.572521000
1	-1.781364000	0.966284000	1.643743000



This geometry is used as starting geometry for locating $(D_1/D_0)_{CI}$.

Preliminary Examination of the Orbitals

{taken from the opt.com file}

```
%chk=opt.com
%mem=600MB
#p UHF/STO-3G Pop=NO NoSymm SCF(MaxCycles=300) Ginput
```

Population analysis of hydrogen transferred form of glycine conformer II

1	2		
1	-0.482837000	1.913743000	1.562767000
8	-1.443892000	1.741919000	-0.727920000
8	-0.414717000	0.086455000	-1.840540000
6	-0.769243000	0.739172000	-0.751830000
6	-0.234797000	0.101986000	0.517907000
1	0.845290000	0.117059000	0.551634000
1	-0.589825000	-0.910434000	0.646507000
7	-0.761548000	0.946481000	1.672427000
1	-0.419351000	0.605454000	2.561240000
1	-1.773735000	0.940348000	1.689594000

Radical cationic glycine possesses 39 electrons and a positive charge. So this is an open shell system and therefore, a UHF or ROHF computation is absolutely necessary to generate the molecular orbitals. Under the unrestricted scheme, population analysis with *Pop = Full* option generates two sets of molecular orbitals associated with α and β spins. It is very difficult to handle two different sets of orbitals in

CASSCF computations. Therefore, we need to generate one set of orbitals for two different spins. One can do it in two different ways: by utilizing (a) UHF natural orbitals, and (b) ROHF canonical orbitals.

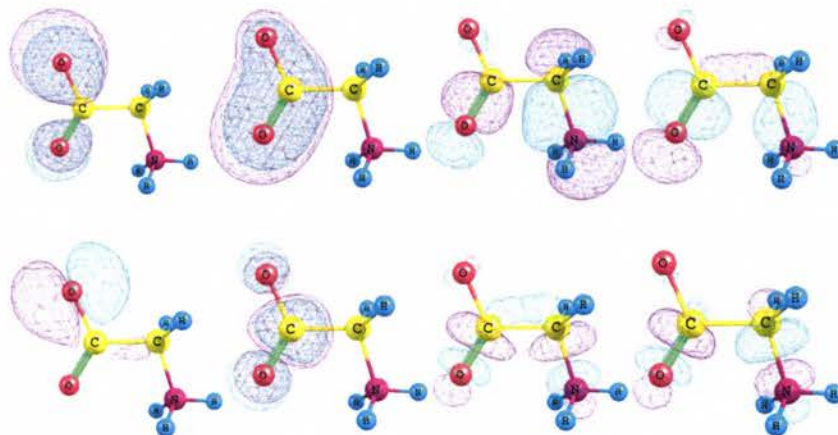


Figure 7: Natural orbitals used in (9,8) active space to compute $(D_1/D_0)_{CI}$ of conformer II

The natural orbitals (NOs) are formed by diagonalizing the one particle density matrix so that they are related to the molecular orbitals; they span the same space and describe the same density, but they are no longer eigenvectors of the SCF equations. Therefore, natural orbitals do not have energy eigenvalues. As they diagonalize the density matrix, the eigenvalues correspond to occupations. A UHF computation using *Pop = NaturalOrbitals* option for an open shell system sum up α and β densities and diagonalizes molecular Hamiltonian so that we get a single set of natural orbitals. In most cases, UHF NOs are less delocalized than the ROHF canonical orbitals. So they are helpful in describing the bonding.

Here only NOs with occupations greater than 0, but less than 2 are selected to construct a (9,8) active space, as illustrated in Figure 6. UHF natural orbital

calculations provide fractional occupation numbers for valence orbitals. The NOs that should be included in a CASSCF wavefunction are those with occupation numbers that differ from zero to two (not empty and doubly occupied).¹ Orbitals must be rechecked to ensure that they are the correct ones to be included in the active space.

Run a CASSCF calculation on the D_0 ground ion state

{taken from the excit2.com file}

```
%mem=200MB
%chk=excit2.chk
#p CASSCF(9,8,NRoot=1)/6-31G* Pop=NaturalOrbitals Ginput NoSymm
Guess=Read SCF(MaxCycles=700)
```

CAS of proton transferred form of conformer II

1	2			
1	-0.482837000	1.913743000	1.562767000	
8	-1.443892000	1.741919000	-0.727920000	
8	-0.414717000	0.086455000	-1.840540000	
6	-0.769243000	0.739172000	-0.751830000	
6	-0.234797000	0.101986000	0.517907000	
1	0.845290000	0.117059000	0.551634000	
1	-0.589825000	-0.910434000	0.646507000	
7	-0.761548000	0.946481000	1.672427000	
1	-0.419351000	0.605454000	2.561240000	
1	-1.773735000	0.940348000	1.689594000	

Run a state-averaged CASSCF calculation for the D_1 excited ion state

{taken from the excit3.com file}

```
%mem=200MB
%chk=excit3.chk
#p CASSCF(9,8,NRoot=2,StateAverage)/6-31G* Pop=NaturalOrbitals Ginput NoSymm
Guess=Read SCF(MaxCycles=700)
```

D_1 excitation of proton transferred form

1	2			
1	-0.482837000	1.913743000	1.562767000	
8	-1.443892000	1.741919000	-0.727920000	
8	-0.414717000	0.086455000	-1.840540000	
6	-0.769243000	0.739172000	-0.751830000	
6	-0.234797000	0.101986000	0.517907000	
1	0.845290000	0.117059000	0.551634000	
1	-0.589825000	-0.910434000	0.646507000	
7	-0.761548000	0.946481000	1.672427000	
1	-0.419351000	0.605454000	2.561240000	
1	-1.773735000	0.940348000	1.689594000	

0.500000 0.500000

Optimization of the $(D_1/D_0)_{CI}$ conical intersection

{taken from the ci3.com file}

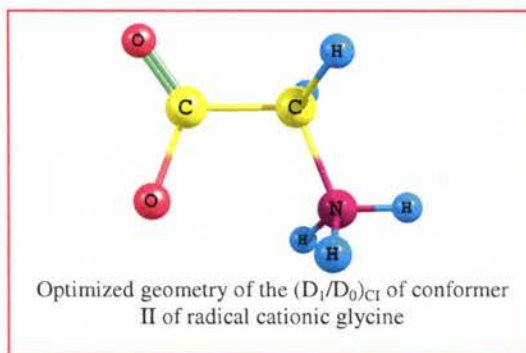
```
%mem=200MB
%chk=ci3.chk
#p CASSCF(9,8,NRoot=2,nocpmcscf)/6-31G* Pop=NaturalOrbitals Gfinput NoSymm
Guess=Read Opt(Conical,MaxCycles=800) SCF(MaxCycles=600,Conver=6)
```

$(D_1/D_0)_{CI}$ from proton transferred form

1	2		
1	-0.482837000	1.913743000	1.562767000
8	-1.443892000	1.741919000	-0.727920000
8	-0.414717000	0.086455000	-1.840540000
6	-0.769243000	0.739172000	-0.751830000
6	-0.234797000	0.101986000	0.517907000
1	0.845290000	0.117059000	0.551634000
1	-0.589825000	-0.910434000	0.646507000
7	-0.761548000	0.946481000	1.672427000
1	-0.419351000	0.605454000	2.561240000
1	-1.773735000	0.940348000	1.689594000

This job optimizes the $(D_1/D_0)_{CI}$ of conformer II of glycine. The Cartesian coordinate of the optimized geometry is as follows:

1	-1.406820000	1.733412000	1.454210000
8	-0.032648000	0.749672000	-2.063765000
8	-1.927724000	1.318406000	-0.892151000
6	-0.638568000	0.855332000	-1.039237000
6	-0.063666000	0.476624000	0.365229000
1	0.802042000	1.082728000	0.589313000
1	0.179474000	-0.575476000	0.397525000
7	-1.143634000	0.756263000	1.453893000
1	-0.782083000	0.516944000	2.369785000
1	-1.976777000	0.208397000	1.280881000



Reference

1. (a) A concise discussion about selection of active space for exemplary systems, benzene and ketene using Gaussian03 can be found in computational photochemistry group (Prof. M. Robb) homepage. (b) see http://www.ch.ic.ac.uk/robb/casscf_ketene_handout.php for selection of NOs of ketene.

APPENDIX VII

Exploration of Potential Energy Surfaces (PESs)

Introduction

Quantum mechanical description of a chemical reaction is expressed as a continuous motion on certain paths of the potential energy surfaces (PESs) connecting reactants with products. In general, reactant and products are considered the minima on the potential energy surface, while an intermediate state, known as the “transition state” would be a saddle point of higher energy. The height of the energy barrier separating reactant and products relates to the overall rate of the reaction, the positions of the minima along the reaction coordinate give the equilibrium geometries of the species, and the relative energies between reactant and products relate to the thermodynamics of the process. All this is known as transition state theory and chemical kinetics.

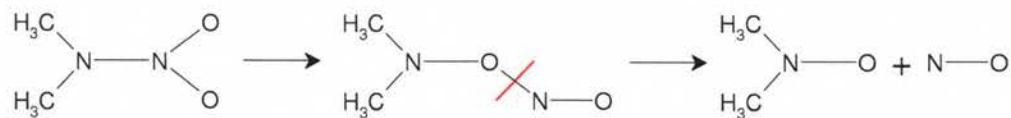
The process of studying a chemical reaction starts by obtaining proper geometries for reactants and products, followed by finding a position of the transition state, and finishes by computing as accurately as possible the relative energies relating the position of the species. To perform geometry optimizations searching for true minima on the PES is by now a well established procedure. A stationary point on the PES is characterized by having all the first derivatives of the energy with respect to each one of the independent coordinates equal to zero and second derivatives larger

than zero. A first order saddle point, on the other hand, has the second derivatives of the energy lower than zero for one coordinate, that is, they are maxima along this coordinate. A transition state is defined as a saddle point having only one negative second derivative along the specific coordinate known as the reaction coordinate. To simplify the treatment, a special set of coordinates known as normal coordinate is defined in a way that the matrix of second derivatives is diagonal. A transition state will have one negative value in the diagonal of such a matrix.

Exploration of potential energy surfaces can be done using *ab-initio* quantum mechanical softwares such as Gaussian03. Here a Gaussian example is given to explicitly discuss the procedure of exploration of PES. In the present appendix, the reaction path for nitro-nitrite isomerization of dimethylnitramine (illustrated below) will be first characterized. Second, a reaction path of internal conversion for DMNA from S_1 excited state to the ground state through $(S_1/S_0)_{CI}$ conical intersection is addressed. The geometries will be obtained at the MP2 and CASSCF levels of theory. The MP2 level of theory is used to compute minima and transition states in the ground state and CASSCF level of theory is used to compute minima and transition states both in the ground and excited state.

Nitro-nitrite Isomerization of DMNA on the Ground State

We are interested in exploring the DMNA potential energy surface to follow reaction path for the nitro-nitrite isomerization.



Undoubtedly many minima and transition states exist on the surface of $(CH_3)_2NNO_2$ - each corresponds to a specific reaction path among the different possible reaction mechanisms described in Chapter 2. Here we consider only the nitro-nitrite isomerization reaction. We want to determine the transition state structure associated with nitro-nitrite isomerization of DMNA (illustrated in the previous page) and to predict the activation energy for the reaction. In order to do so, we need following information:

- ❖ The geometries of $(CH_3)_2NNO_2$ (nitro form) and $(CH_3)_2NONO$ (nitrite form) and their zero-point corrected energies.
- ❖ The geometry of the transition state structure and its zero-point corrected energy.

Optimization of $(CH_3)_2NNO_2$

Starting geometry is obtained from ChemCraft. Here is the input file for the optimization of $(CH_3)_2NNO_2$ at MP2/6-31G(d) level of theory.

(taken from the opt.com file)

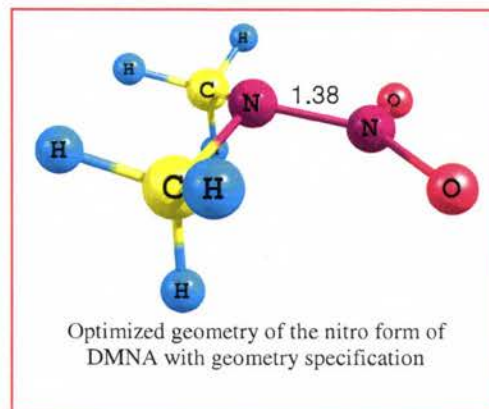
```
%chk=opt
%mem=600MB
#p MP2/6-31G(d) Opt Freq NoSymm
```

Optimization of DMNA (nitro)

```
0      1
7      0.174720000    0.609671000    0.000000000
7      -0.556243127   -0.651869107   -0.013079338
8      -0.807016000   -1.077164000    1.105820000
8      -0.807016000   -1.077164000   -1.105820000
6      0.866990482    0.893108496    1.210423675
6      0.882512498    0.900035176   -1.201968941
1      1.315352000    1.881243000    1.150099000
1      0.153307000    0.898374000    2.069856000
1      1.652750000    0.153147000    1.464063000
1      1.315352000    1.881243000   -1.150099000
1      0.153307000    0.898374000   -2.069856000
1      1.652750000    0.153147000   -1.464063000
```

This optimizes nitro form of DMNA on the S_0 surface. The Cartesian coordinate of the optimized geometry is as follows:

7	0.174720000	0.609671000	0.000000000
7	-0.508704000	-0.600041000	0.000000000
8	-0.807016000	-1.077164000	1.105820000
8	-0.807016000	-1.077164000	-1.105820000
6	0.869661000	0.891438000	1.251787000
6	0.869661000	0.891438000	-1.251787000
1	1.315352000	1.881243000	1.150099000
1	0.153307000	0.898374000	2.069856000
1	1.652750000	0.153147000	1.464063000
1	1.315352000	1.881243000	-1.150099000
1	0.153307000	0.898374000	-2.069856000
1	1.652750000	0.153147000	-1.464063000



The zero point corrected MP2 energy for the nitro form of DMNA is predicted to be -338.567797 Hartree. The structure of nitro form shows a planar N-NO₂ moiety.

Optimization of $(CH_3)_2NONO$

Nitrite form can have two isomers: cis and trans. Here only cis isomer of the nitrite form is considered. Starting geometry for cis isomer of the nitrite form is obtained from ChemCraft and the input file for the optimization of this form at MP2/6-31G(d) level of theory is given below.

(taken from the opt1.com file)

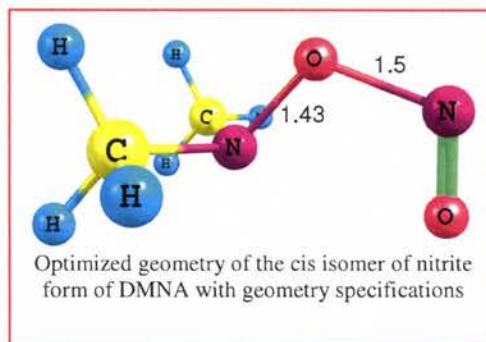
```
%chk=opt1
%mem=600MB
#p MP2/6-31G(d) Opt Freq NoSymm
```

Optimization of DMNA (nitrite)

0	1		
7	0.568304000	0.217306000	-0.185643000
7	-1.839234375	-0.167342949	0.212689303
8	-0.425208079	-0.097707096	0.866092706
8	-1.819379000	0.039625000	-0.938510000
6	1.142000107	1.456271105	0.203148385
6	1.502829000	-0.904618000	-0.171059000
1	1.854410223	1.673247715	-0.473618657
1	0.434945000	2.251422000	0.239782000
1	1.673744000	1.401950000	1.208694000
1	2.263744000	-0.716524000	-0.933267000
1	0.958626000	-1.813390000	-0.431114000
1	1.987828000	-1.035912000	0.806330000

This optimizes nitro form of DMNA on the S_0 surface. The Cartesian coordinate of the optimized geometry is as follows:

7	0.568304000	0.217306000	-0.185643000
7	-1.783024000	-0.150885000	0.227242000
8	-0.399988000	-0.074418000	0.824746000
8	-1.819379000	0.039625000	-0.938510000
6	1.196766000	1.471073000	0.221039000
6	1.502829000	-0.904618000	-0.171059000
1	1.948828000	1.727702000	-0.529875000
1	0.434945000	2.251422000	0.239782000
1	1.673744000	1.401950000	1.208694000
1	2.263744000	-0.716524000	-0.933267000
1	0.958626000	-1.813390000	-0.431114000
1	1.987828000	-1.035912000	0.806330000



Optimization of TS associated with nitro-nitrite isomerization

The nitro-nitrite isomerization is a thermochemically allowed decomposition mechanism of DMNA in the ground electronic state. The nature of the transition state (TS) associated with the nitro-nitrite isomerization channel is a subject of considerable discussion. Both tight and loose TS geometries are reported in the literature for the nitro-nitrite isomerization in the ground state (see chapter 2). A tight TS geometry corresponds to an isomerization for which rotation of NO_2 is substantial at short N-N bond length. A loose TS geometry, on the other hand, corresponds to an isomerization for which rotation of NO_2 does not happen until the N-N bond is elongated substantially.

Both tight (with a short N-N bond distance) and loose (with a long N-N bond distance) TSs on the ground electronic state surface of DMNA at the MP2/6-31G(d) level of theory are optimized.

Optimization of tight TS

Here is the input file for the optimization of tight transition state associated with nitro-nitrite isomerization computed at the MP2/6-31G(d) level of theory.

(taken from the ts1.com file)

```
%chk=ts1
%mem=600MB
#p MP2/6-31G(d) Opt=(TS,NoEigen,MaxCycles=600,CalcFC) Freq NoSymm
```

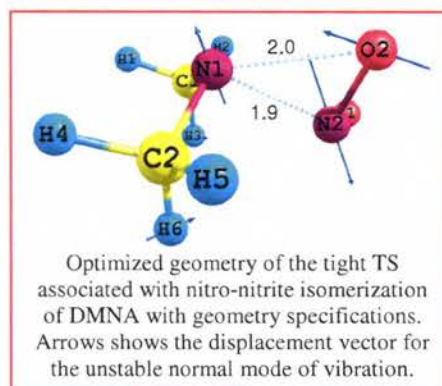
Optimization of tight TS associated with nitro-nitrite isomerization

```
0 1
7 0.792536636 -0.049896588 -0.417893893
7 -1.008145692 -0.264052406 0.414748662
8 -1.805520000 0.605201000 0.390900000
8 -0.959110309 -1.131004836 -0.689265465
6 0.838018000 1.392425000 -0.257453000
6 1.590942000 -0.780726000 0.488196000
1 1.821670000 1.690395000 -0.651292000
1 0.076411000 1.876490000 -0.869919000
1 0.743450000 1.709165000 0.789073000
1 2.630457000 -0.691149000 0.139554000
1 1.297036562 -1.826579470 0.392582919
1 1.510576000 -0.414137000 1.518532000
```

This optimizes tight TS for nitro-nitrite isomerization of DMNA on the S_0 surface. The

Cartesian coordinate of the optimized geometry is as follows:

```
7 0.802668000 -0.037587000 -0.469189000
7 -0.926176000 -0.231040000 0.388917000
8 -1.805520000 0.605201000 0.390900000
8 -0.919056000 -1.121430000 -0.663563000
6 0.838018000 1.392425000 -0.257453000
6 1.590942000 -0.780726000 0.488196000
1 1.821670000 1.690395000 -0.651292000
1 0.076411000 1.876490000 -0.869919000
1 0.743450000 1.709165000 0.789073000
1 2.630457000 -0.691149000 0.139554000
1 1.304845000 -1.830737000 0.432806000
1 1.510576000 -0.414137000 1.518532000
```



In the tight transition state, the N1N2 bond distance is predicted to be 1.9 Å, and N1O2 is predicted to be 2.0 Å. The zero point corrected MP2 energy is predicted to be -338.424884 Hartree. Thus the activation energy at the MP2/6-31G(d) level is calculated to be [-338.424884-(-338.567797)] Hartree or 90 kcal/mol.

Optimization of loose TS

Here is the input file for the optimization of tight transition state associated with nitro-nitrite isomerization computed at the MP2/6-31G(d) level of theory.

(taken from the ts2.com file)

```
%chk=ts2
%mem=600MB
#p MP2/6-31G(d) Opt=(TS,NoEigen,MaxCycles=600,CalcFC) Freq NoSymm
```

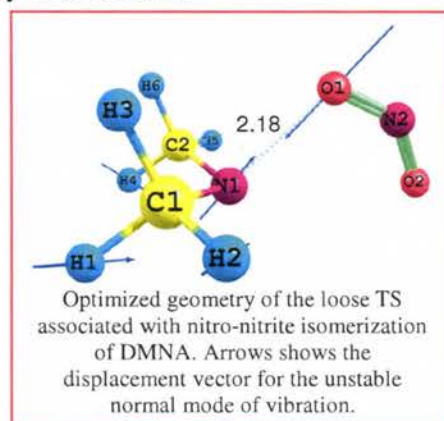
Optimization of loose TS associated with nitro-nitrite isomerization

```
0 1
7 0.734293605 0.278491316 -0.497878112
7 -2.008000013 -0.196104507 0.124689191
8 -1.102382388 -0.192129303 0.846979908
8 -2.381760151 -0.064308164 -0.987138164
6 1.279936632 1.446867658 0.159529849
6 1.592292632 -0.852964507 -0.217746151
1 2.240858947 1.751419125 -0.293606875
1 0.594762138 2.299168493 0.053968013
1 1.485944178 1.317393342 1.242048671
1 2.579254770 -0.739180796 -0.702285862
1 1.148383138 -1.776591671 -0.614724987
1 1.803579013 -1.021151507 0.858277836
```

This optimizes tight TS for nitro-nitrite isomerization of DMNA on the S_0 surface. The

Cartesian coordinate of the optimized geometry is as follows:

```
7 0.721213000 0.274754000 -0.486199000
7 -2.010803000 -0.197506000 0.129828000
8 -1.078557000 -0.185589000 0.827359000
8 -2.378490000 -0.063841000 -0.986671000
6 1.272462000 1.444999000 0.162800000
6 1.584818000 -0.854366000 -0.214476000
1 2.229647000 1.742543000 -0.302483000
1 0.588689000 2.297767000 0.056771000
1 1.488280000 1.319262000 1.242983000
1 2.565707000 -0.731239000 -0.708359000
1 1.142310000 -1.777526000 -0.611922000
1 1.806382000 -1.022553000 0.858745000
```



In the loose transition state geometry, the N1N2 bond distance is predicted to be 2.8 Å, and N1O1 bond distance is predicted to be 2.3 Å. The activation energy barrier of the loose TS is calculated to be 69 kcal/mol, significantly lower in energy than that of tight TS at the MP2/6-31G(d) level.

Exploring PES associated with tight nitro-nitrite isomerization TS:

IRC job enables us to verify that the tight TS structure connects the two minima corresponding to nitro and nitrite forms, respectively. It also explores that full reaction path for nitro-nitrite isomerization through a tight TS.

Here is the input file for the IRC calculation for nitro-nitrite isomerization through a tight TS computed at the MP2/6-31G(d) level of theory.

(taken from the irc1.com file)

```
%chk=irc1
%mem=600MB
#p MP2/6-31G(d) IRC=(CalcFC,MaxPoints=10,MaxCycle=200) NoSymm
```

IRC calculation for nitrite nitrate isomerization through tight TS from ts1.log

```
0 1
7 -0.146363000 0.786991000 -0.474395000
7 -0.050206000 -0.749041000 0.706297000
8 0.971942000 -1.229299000 1.150272000
8 -0.630316000 0.263114000 1.440853000
6 1.124261000 0.489369000 -1.097250000
6 -1.284909000 0.369454000 -1.261538000
1 1.221956000 1.263255000 -1.873796000
1 1.932190000 0.637382000 -0.379737000
1 1.196221000 -0.506874000 -1.552009000
1 -1.407439000 1.147571000 -2.029450000
1 -2.169416000 0.379937000 -0.625158000
1 -1.166651000 -0.610374000 -1.739442000
```

IRC calculation produces a table summarizing the results just before exiting. Here is the table for the present calculation:

SUMMARY OF REACTION PATH FOLLOWING: (Int. Coord: Angstroms, and Degrees)					
	ENERGY	RX.COORD	X1	Y1	Z1
1	-338.53297	-.99918	-.16935	.84288	-.45531
2	-338.53094	-.89919	-.16726	.83876	-.45772
3	-338.52893	-.79920	-.16517	.83444	-.45999
4	-338.52696	-.69922	-.16310	.82992	-.46213
5	-338.52505	-.59923	-.16103	.82522	-.46412
6	-338.52322	-.49925	-.15897	.82034	-.46596
7	-338.52150	-.39929	-.15691	.81538	-.46772
8	-338.51993	-.29930	-.15487	.81026	-.46933
9	-338.51856	-.19931	-.15284	.80501	-.47081
10	-338.51746	-.09932	-.15083	.79961	-.47211
11	-338.51630	.00000	-.14636	.78699	-.47440
12	-338.51769	.09932	-.14189	.77420	-.47656
13	-338.51920	.19929	-.13995	.76854	-.47739
14	-338.52125	.29929	-.13813	.76314	-.47797
15	-338.52379	.39929	-.13634	.75788	-.47859
16	-338.52672	.49928	-.13457	.75275	-.47924

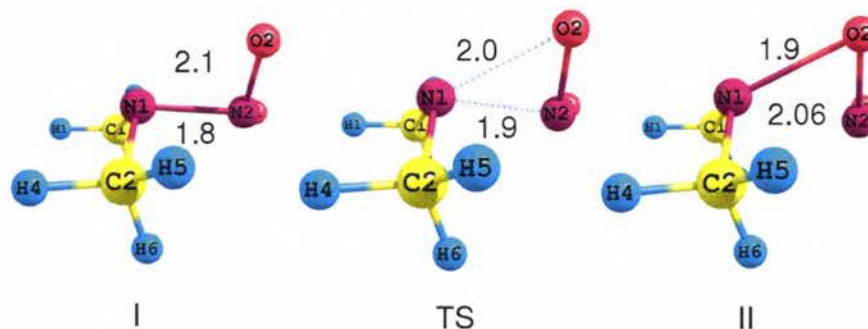
17	-338.52998	.59928	-.13282	.74776	-.47995
18	-338.53349	.69928	-.13108	.74288	-.48070
19	-338.53718	.79927	-.12935	.73810	-.48150
20	-338.54100	.89927	-.12763	.73339	-.48232
21	-338.54491	.99927	-.12591	.72875	-.48315
	X2	Y2	Z2	X3	Y3
1	-.05988	-.85561	.71033	.98522	-1.22399
2	-.05898	-.84731	.70917	.98399	-1.22405
3	-.05807	-.83875	.70814	.98275	-1.22418
4	-.05716	-.82992	.70725	.98152	-1.22440
5	-.05624	-.82084	.70651	.98029	-1.22470
6	-.05534	-.81153	.70592	.97907	-1.22509
7	-.05444	-.80210	.70542	.97786	-1.22552
8	-.05356	-.79246	.70508	.97667	-1.22603
9	-.05269	-.78265	.70488	.97549	-1.22662
10	-.05187	-.77260	.70494	.97436	-1.22732
11	-.05021	-.74904	.70630	.97194	-1.22930
12	-.04854	-.72544	.70754	.96957	-1.23133
13	-.04784	-.71503	.70823	.96855	-1.23226
14	-.04726	-.70433	.71013	.96752	-1.23332
15	-.04670	-.69359	.71228	.96650	-1.23442
16	-.04608	-.68287	.71464	.96542	-1.23553
17	-.04537	-.67218	.71718	.96427	-1.23663
18	-.04455	-.66155	.71986	.96305	-1.23771
19	-.04358	-.65098	.72265	.96173	-1.23877
20	-.04245	-.64049	.72550	.96031	-1.23979
21	-.04114	-.63010	.72838	.95879	-1.24077
	Z3	X4	Y4	Z4	X5
1	1.16617	-.60308	.30498	1.37383	1.11486
2	1.16495	-.60587	.30152	1.38132	1.11594
3	1.16371	-.60859	.29800	1.38852	1.11697
4	1.16243	-.61123	.29442	1.39543	1.11795
5	1.16111	-.61380	.29079	1.40202	1.11888
6	1.15976	-.61629	.28711	1.40831	1.11976
7	1.15838	-.61874	.28341	1.41443	1.12059
8	1.15697	-.62111	.27966	1.42024	1.12139
9	1.15552	-.62342	.27587	1.42576	1.12214
10	1.15402	-.62563	.27204	1.43086	1.12284
11	1.15027	-.63032	.26311	1.44085	1.12426
12	1.14658	-.63497	.25425	1.45073	1.12559
13	1.14492	-.63696	.25035	1.45485	1.12615
14	1.14289	-.63878	.24617	1.45805	1.12682
15	1.14078	-.64059	.24192	1.46111	1.12754
16	1.13859	-.64240	.23763	1.46411	1.12829
17	1.13632	-.64425	.23330	1.46710	1.12910
18	1.13397	-.64615	.22896	1.47011	1.12995
19	1.13154	-.64812	.22462	1.47318	1.13086
20	1.12903	-.65017	.22030	1.47634	1.13183
21	1.12644	-.65232	.21603	1.47962	1.13286
	Y5	Z5	X6	Y6	Z6
1	.48842	-1.07248	-1.28818	.37022	-1.25203
2	.48814	-1.07504	-1.28772	.36994	-1.25297
3	.48793	-1.07752	-1.28730	.36971	-1.25389
4	.48779	-1.07993	-1.28691	.36951	-1.25479
5	.48772	-1.08227	-1.28656	.36936	-1.25567
6	.48769	-1.08451	-1.28625	.36921	-1.25651
7	.48779	-1.08676	-1.28594	.36917	-1.25738
8	.48789	-1.08891	-1.28567	.36911	-1.25821
9	.48808	-1.09099	-1.28543	.36911	-1.25902
10	.48836	-1.09299	-1.28524	.36915	-1.25981
11	.48937	-1.09725	-1.28491	.36945	-1.26154
12	.49048	-1.10145	-1.28460	.36983	-1.26326
13	.49103	-1.10327	-1.28446	.37005	-1.26401

14	.49162	-1.10504	-1.28436	.37022	-1.26471
15	.49217	-1.10681	-1.28428	.37035	-1.26541
16	.49270	-1.10858	-1.28420	.37044	-1.26609
17	.49319	-1.11038	-1.28412	.37050	-1.26678
18	.49363	-1.11221	-1.28404	.37050	-1.26747
19	.49405	-1.11408	-1.28396	.37047	-1.26817
20	.49442	-1.11599	-1.28389	.37038	-1.26887
21	.49476	-1.11796	-1.28381	.37027	-1.26959
	X7	Y7	Z7	X8	Y8
1	1.20920	1.25146	-1.85861	1.93141	.64131
2	1.20977	1.25302	-1.85968	1.93191	.64088
3	1.21038	1.25453	-1.86076	1.93231	.64048
4	1.21107	1.25597	-1.86187	1.93261	.64012
5	1.21185	1.25731	-1.86302	1.93282	.63977
6	1.21279	1.25880	-1.86450	1.93283	.63940
7	1.21372	1.25965	-1.86543	1.93302	.63911
8	1.21487	1.26081	-1.86688	1.93295	.63876
9	1.21610	1.26171	-1.86824	1.93288	.63846
10	1.21751	1.26249	-1.86974	1.93270	.63816
11	1.22196	1.26326	-1.87380	1.93219	.63738
12	1.22669	1.26379	-1.87788	1.93156	.63657
13	1.22899	1.26376	-1.87968	1.93133	.63616
14	1.23153	1.26345	-1.88181	1.93137	.63572
15	1.23390	1.26313	-1.88387	1.93146	.63536
16	1.23618	1.26283	-1.88595	1.93162	.63503
17	1.23832	1.26251	-1.88796	1.93185	.63475
18	1.24033	1.26228	-1.89002	1.93212	.63450
19	1.24219	1.26202	-1.89198	1.93250	.63429
20	1.24392	1.26190	-1.89404	1.93288	.63412
21	1.24549	1.26171	-1.89597	1.93340	.63400
	Z8	X9	Y9	Z9	X10
1	-.36542	1.17033	-.51415	-1.51562	-1.40710
2	-.36728	1.17293	-.51366	-1.51967	-1.40695
3	-.36902	1.17550	-.51313	-1.52357	-1.40678
4	-.37064	1.17803	-.51256	-1.52731	-1.40661
5	-.37212	1.18049	-.51196	-1.53089	-1.40645
6	-.37358	1.18287	-.51107	-1.53418	-1.40638
7	-.37476	1.18525	-.51074	-1.53766	-1.40626
8	-.37598	1.18752	-.50994	-1.54075	-1.40626
9	-.37704	1.18974	-.50926	-1.54378	-1.40629
10	-.37798	1.19185	-.50853	-1.54651	-1.40641
11	-.37974	1.19622	-.50687	-1.55201	-1.40744
12	-.38133	1.20042	-.50523	-1.55742	-1.40863
13	-.38197	1.20225	-.50458	-1.55978	-1.40929
14	-.38275	1.20423	-.50394	-1.56189	-1.41016
15	-.38355	1.20624	-.50336	-1.56392	-1.41090
16	-.38441	1.20835	-.50279	-1.56598	-1.41160
17	-.38530	1.21053	-.50227	-1.56806	-1.41219
18	-.38628	1.21280	-.50172	-1.57017	-1.41269
19	-.38729	1.21516	-.50124	-1.57235	-1.41305
20	-.38842	1.21760	-.50070	-1.57454	-1.41333
21	-.38957	1.22013	-.50025	-1.57684	-1.41346
	Y10	Z10	X11	Y11	Z11
1	1.12753	-2.03995	-2.18467	.38190	-.63355
2	1.12985	-2.03853	-2.18307	.38155	-.63280
3	1.13212	-2.03716	-2.18152	.38126	-.63206
4	1.13432	-2.03585	-2.18000	.38101	-.63130
5	1.13641	-2.03463	-2.17853	.38080	-.63054
6	1.13859	-2.03372	-2.17692	.38062	-.62991
7	1.14026	-2.03241	-2.17576	.38047	-.62897
8	1.14213	-2.03157	-2.17433	.38034	-.62826
9	1.14377	-2.03072	-2.17305	.38023	-.62748
10	1.14527	-2.03005	-2.17182	.38015	-.62673

11	1.14757	-2.02945	-2.16942	.37994	-.62516
12	1.14964	-2.02898	-2.16706	.37975	-.62353
13	1.15027	-2.02887	-2.16613	.37965	-.62284
14	1.15054	-2.02909	-2.16545	.37945	-.62242
15	1.15079	-2.02923	-2.16481	.37930	-.62201
16	1.15106	-2.02937	-2.16416	.37914	-.62163
17	1.15130	-2.02940	-2.16355	.37899	-.62125
18	1.15164	-2.02945	-2.16287	.37885	-.62091
19	1.15191	-2.02933	-2.16226	.37871	-.62052
20	1.15237	-2.02928	-2.16151	.37856	-.62022
21	1.15271	-2.02899	-2.16089	.37841	-.61981
	X12	Y12	Z12		
1	-1.15062	-.61934	-1.70429		
2	-1.15208	-.61862	-1.70791		
3	-1.15356	-.61788	-1.71145		
4	-1.15505	-.61712	-1.71489		
5	-1.15653	-.61634	-1.71823		
6	-1.15802	-.61532	-1.72135		
7	-1.15943	-.61479	-1.72467		
8	-1.16087	-.61386	-1.72768		
9	-1.16228	-.61305	-1.73068		
10	-1.16365	-.61221	-1.73349		
11	-1.16665	-.61037	-1.73944		
12	-1.16952	-.60856	-1.74531		
13	-1.17084	-.60785	-1.74792		
14	-1.17247	-.60720	-1.75043		
15	-1.17409	-.60662	-1.75288		
16	-1.17581	-.60607	-1.75536		
17	-1.17760	-.60554	-1.75786		
18	-1.17945	-.60502	-1.76039		
19	-1.18138	-.60453	-1.76296		
20	-1.18336	-.60403	-1.76556		
21	-1.18540	-.60355	-1.76820		

The entries in the table are arranged in order of increasing reaction coordinate or distance along the reaction path (the reaction coordinate is a composite variable spanning all of the degrees of freedom of the potential energy surface). The energy and optimized variable values are listed for each point (in this case, as Cartesian coordinates). The first and last entries correspond to the structure on each side of the reaction path. An IRC calculation does not necessarily step all the way down to the minimum (reactant and product). Here for the above example the calculation takes 10 steps in each direction, where each step corresponds to a geometry optimization.

Here are the two structures produced by the present calculation, along with the transition structure from which the IRC began:



Structure I (numbered 21 in IRC output), we find a nitro-like structure, although the N1N2 bond distance is elongated and N-NO₂ moiety is not planar: we can identify the minimum along this side of the path as nitro form. In structure II (numbered 10 in the IRC output), the N1N2 bond length is elongated and N1O2 bond length is contracted. Both changes are what one would expect as DMNA (nitro form) isomerizes to the nitrite form.

Plotting reaction path associated with nitro-nitrite isomerization through tight TS

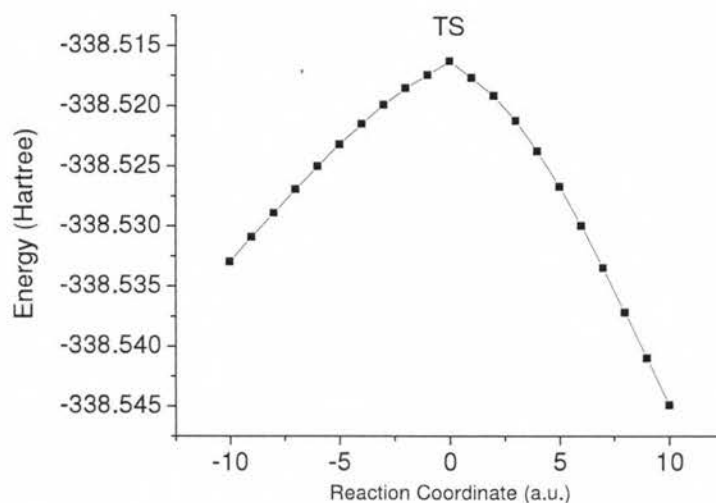


Figure 1: Reaction path from nitro-nitrite isomerization TS, computed at MP2/6-31G(d) level of theory using IRC algorithm as implemented in Gaussian03.

The above diagram illustrates the results we have computed for the PES of the nitro-nitrite isomerization of DMNA through a tight TS computed at the MP2/6-31G(d) level of theory. Here only 10 steps are computed in each direction. Therefore, two minimum points in the figure do not correspond to the nitro and nitrite form.

Exploring PES associated with loose nitro-nitrite isomerization TS

One can find out the reaction path associated with loose nitro-nitrite isomerization TS following the procedure mentioned above; however, the primary difficulty to explore PES using IRC in this case is that the nitro-nitrite isomerization through a loose geometry occurs through two steps: (1) initial elongation of N-NO₂ bond and; (2) final formation of N-ONO bond. This information is obtained after an extensive theoretical work on this system. The loose TS geometry associated with nitro-nitrite isomerization corresponds to the TS associated with formation of N-ONO bond. Therefore, if we run an IRC calculation, the forward direction of this reaction path will find one minimum corresponding to nitrite form, but backward direction of this reaction path will reach a dissociation product. In order to explore the reaction path for nitro-nitrite isomerization through a loose geometry, we need to scan N-NO₂ bond and N-ONO bond. We find that the N-NO₂ bond elongation reaction coordinate does not have a transition state; however, N-ONO bond contraction reaction coordinate possesses a transition state which is designated as loose TS associated with nitro-nitrite isomerization.

N-NO₂ bond scan

Here is the input file for the PES scan of N-NO₂ bond of DMNA computed at the CASSCF(14,11)/6-31G(d) level of theory. This calculation could be performed at

MP2/6-31G(d) level of theory and in that case the input lines are same as that of CASSCF level of theory. Molecular geometry must be represented here at Z-matrix form.

(taken from the scan1.com file)

```
%chk=scan1.chk
%mem=300MB
#p CASSCF(14,11)/6-31G* Guess=Read SCF(MaxCycles=900)
Pop=Full Gfinput NoSymm Opt=(Z-Matrix,MaxCycles=900)
```

N-NO₂ bond elongation scan

```
0 1
8
7 1 R1
8 2 R2      1 A123
7 2 r      3 ang1      1 dia1
6 4 R4      2 ang2      1 -D1245
6 4 R5      2 ang3      1 -D1246
1 5 R51     4 ang4      2 -D2457
1 5 R6      4 ang5      2 D2458
1 5 R7      4 ang6      2 dia2
1 6 R8      4 ang7      2 dia3
1 6 R9      4 ang8      2 D2459
1 6 R10     4 ang9      2 -D24510
```

Variables:

```
r      = 1.45600 S 20 0.1
R1     = 1.22232195
R2     = 1.22232195
A123   = 126.39870378
R4     = 1.45441317
R5     = 1.45441317
D1245  = 26.24753338
D1246  = 156.76794153
R51    = 1.08195985
R6     = 1.08195985
R7     = 1.08195985
R8     = 1.08195985
R9     = 1.08195985
R10    = 1.08195985
D2457  = 61.20810212
D2458  = 61.20810212
D2459  = 61.20810212
D24510 = 61.20810212
ang1   = 116.761313
ang2   = 111.751966
ang3   = 111.752051
ang4   = 112.833390
ang5   = 110.186844
ang6   = 106.889505
ang7   = 106.889423
ang8   = 112.833394
ang9   = 110.186850
dia1   = 176.654722
dia2   = 176.674519
dia3   = -176.674339
```

The above PES scan calculation optimizes all the geometrical variables of DMNA except for the N-NO₂ bond distance (represented as r in the above input line). The calculated energies are plotted below with respect to their N-NO₂ bond distance (r in Å).

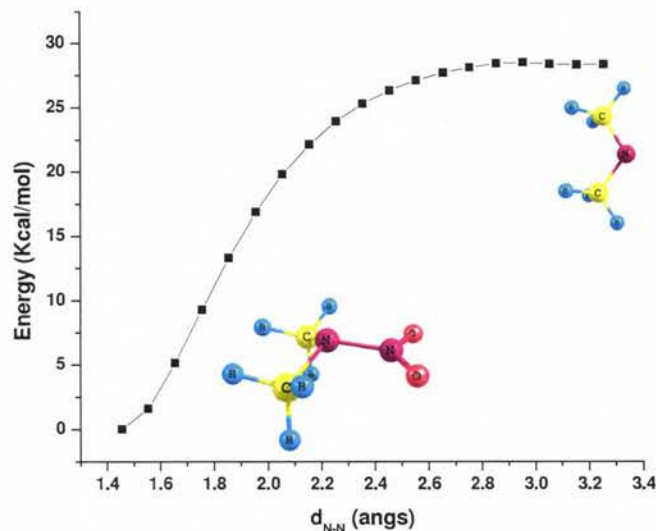


Figure 2: Potential energy surface scan of N-NO₂ bond elongation reaction coordinate at the CASSCF(14,11)/6-31G(d) level of theory.

N-ONO bond scan

Here is the input file for the PES scan of N-ONO bond of DMNA computed at the CASSCF(12,9)/6-31G(d) level of theory.

(taken from the scan2.com file)

```
%chk=scan2.chk
%mem=300MB
#p CASSCF(12,9)/6-31G* SCF(MaxCycles=700) Guess=Read
Pop=Full Ginput NoSymm Opt=(Z-Matrix,MaxCycles=600)
```

N-ONO bond contraction scan

```
0 1
8
7 1 R12
8 2 R23 1 A123
7 3 r 2 al 1 dl
```

6	4	R4	3	A345	2	d2
6	4	R45	5	a2	3	d3
1	6	R67	4	a3	5	d4
1	6	R61	4	a4	3	d5
1	6	R62	4	a5	3	D3469
1	5	R63	4	a6	6	d6
1	5	R64	4	a7	3	d7
1	5	R65	4	a8	6	d8

Variables:

r 1.46908443 S 20 0.1

R12 1.18175546

R23 1.46908443

A123 114.24750051

R45 1.46020868

R4 1.46020868

A345 105.65285952

R67 1.09433784

R61 1.09433784

R62 1.09433784

R63 1.09433784

R64 1.09433784

R65 1.09433784

D3469 59.06099873

a1 110.562203

a2 112.428148

a3 108.570088

a4 107.835581

a5 112.527189

a6 108.570458

a7 107.836355

a8 112.526318

d1 0.006820

d2 -120.317676

d3 114.759140

d4 -176.982935

d5 179.901623

d6 176.984219

d7 -179.901321

d8 55.698957

The above PES scan calculation optimizes all the geometrical variables of nitrite form except for the N-ONO bond distance (represented as r in the above input line). The nitrite form is taken as the initial geometry and N-ONO bond is stretched during the present scan. Reverse direction of this N-ONO bond elongation coordinate represents N-ONO bond contraction reaction coordinate of DMNA. The calculated energies are plotted below with respect to their N-ONO bond distance (r in Å).

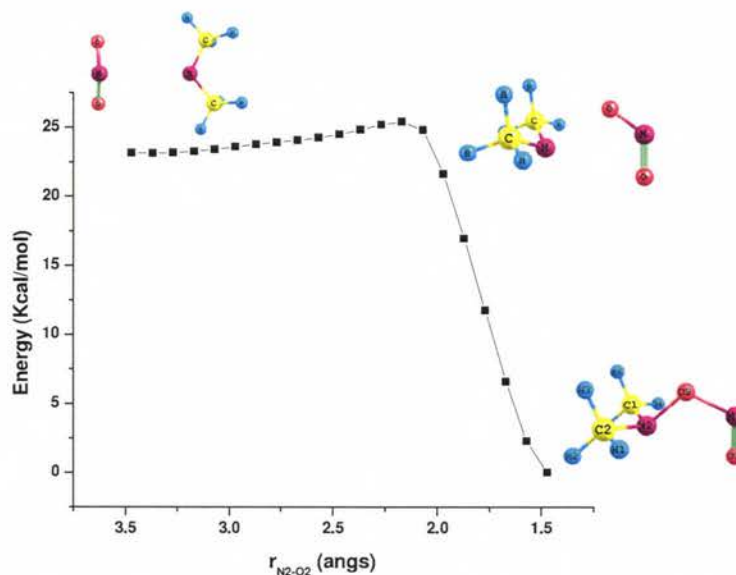


Figure 3: Potential energy surface scan along the N-ONO bond contraction reaction coordinate of DMNA.

Exploring $S_1(n,\pi^*)$ potential energy surface of DMNA

IRC algorithm can be used to explore excited electronic state potential energy surfaces. One requirement to do that is to start with a geometry which is at the uphill on a potential energy surface, such as TS, FC geometry, or a high-lying conical intersection. In the following example we show how to explore S_1 excited state surface from the FC point of S_1 state to the $(S_1/S_0)_{CI}$, and from $(S_1/S_0)_{CI}$ to the FC point of ground state surface.

From the FC point to the $(S_1/S_0)_{CI}$

IRC calculation requires initial force constant, which cannot be calculated with an active space containing more than 8 orbitals using Gaussian03. Therefore, to run an IRC calculation at a CASSCF(14,11) level of theory, the initial force constant is first calculated at a CASSCF(10,7) level of theory and then is used in CASSCF(14,11) calculation. To read force constant from previous checkpoint file, $IRC = RCFC$

keyword is used. Here is the input file for the IRC calculation to explore S_1 PES from the FC point of S_1 state to the $(S_1/S_0)_{CI}$ conical intersection computed at the CASSCF(14,11)/6-31G(d) level of theory.

(taken from the irc4.com file)

```
%chk=irc4
%mem=600MB
#p CASSCF(14,11,NRoot=2)/6-31G(d) IRC=(RCFC,MaxPoints=30,MaxCycle=200) NoSymm
```

IRC calculation from FC point to the $(S_1/S_0)_{CI}$

0	1		
7	0.000000000	0.606152000	-0.358763000
7	-0.000001000	-0.292338000	0.786631000
8	1.091020000	-0.609441000	1.237397000
8	-1.091022000	-0.609439000	1.237398000
6	1.226870000	0.494013000	-1.131766000
6	-1.226869000	0.494012000	-1.131766000
1	1.169349000	1.230610000	-1.920793000
1	2.078358000	0.720773000	-0.512500000
1	1.357871000	-0.490712000	-1.575317000
1	-1.169348000	1.230606000	-1.920796000
1	-2.078357000	0.720774000	-0.512501000
1	-1.357871000	-0.490715000	-1.575314000

From the $(S_1/S_0)_{CI}$ to the FC point of the ground state

Here is the input file for the IRC calculation to explore S_0 PES from the $(S_1/S_0)_{CI}$ conical intersection to the FC point of the ground state computed at the CASSCF(14,11)/6-31G(d) level of theory.

(taken from the irc5.com file)

```
%chk=irc5
%mem=600MB
#p CASSCF(14,11,NRoot=1)/6-31G(d) IRC=(RCFC,MaxPoints=30,MaxCycle=200,Backward) NoSymm
```

IRC calculation from FC point to the $(S_1/S_0)_{CI}$

0	1		
7	0.000000000	0.606152000	-0.358763000
7	-0.000001000	-0.292338000	0.786631000
8	1.091020000	-0.609441000	1.237397000
8	-1.091022000	-0.609439000	1.237398000
6	1.226870000	0.494013000	-1.131766000
6	-1.226869000	0.494012000	-1.131766000
1	1.169349000	1.230610000	-1.920793000
1	2.078358000	0.720773000	-0.512500000
1	1.357871000	-0.490712000	-1.575317000
1	-1.169348000	1.230606000	-1.920796000
1	-2.078357000	0.720774000	-0.512501000

1 -1.357871000 -0.490715000 -1.575314000

The above two IRC calculations explore portion of PES which can allow ultrafast internal conversion of DMNA from S_1 state. Full reaction paths are illustrated below plotting the computed energies from the above two calculations.

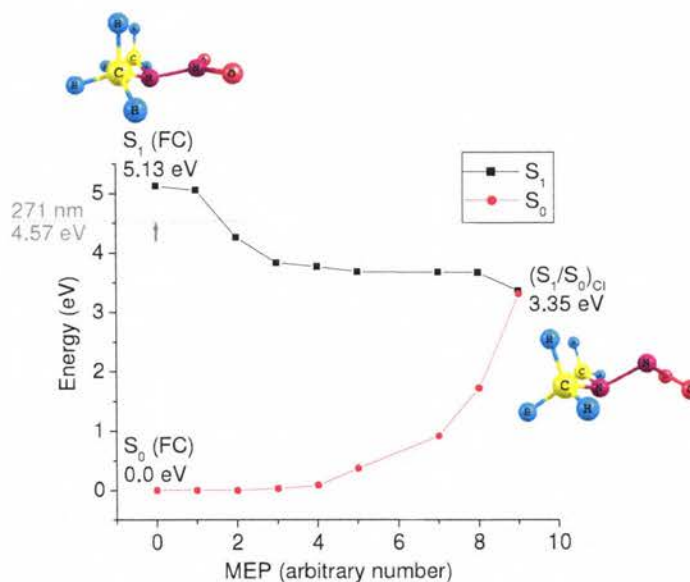


Figure 3: Reaction path from FC point to the $(S_1/S_0)_{CI}$ conical intersection following S_1 and S_0 energy gradients of DMNA, computed using IRC algorithm at CASSCF(14,11)/6-31G(d) level of theory.

Final Remarks on IRC calculations Based on Experience:

Although IRC algorithm and PES scan, as implemented in Gaussian03, is a powerful technique to explore PES, a number of limitations of this method are found:

1. While exploring excited electronic state ($NRoot \geq 2$) PES using IRC algorithm at the CASSCF level of theory, considerable care must be exercised. IRC calculation requires initial force constant which can be obtained by *CalcFC* keyword. Now if one has to explore PES for $NRoot = 2$, one, in principle, can use *CalcFC* keyword directly and run IRC calculation. However, most of the

time, SCF convergence failure problem appears in those cases and a state averaged calculation is required to run IRC calculation for $NRoot \geq 2$. If *CalcFC* keyword is used, Gaussian03 can not do state average calculation. *CalcAll* (which calculates force constant in each step of optimization) is absolutely necessary to run state averaged IRC calculation. This problem is a bug in the system, which makes the IRC calculation for $NRoot \geq 2$ very expensive.

2. The IRC calculation provides a convenient description of the progress of a reaction and does not necessarily stop all the way to the minimum. IRC calculation takes specified number of steps in each direction. Sometimes, if one starts with an FC geometry on the excited electronic potential energy surface, one can find a number of directions because FC geometry is not a stable minimum or TS on the excited electronic state PES. One can fix each direction by specifying the Phase. A detailed discussion about Phase is given in Gaussian03 manual.
3. PES scan explores the PES along a particular normal reaction coordinate (bond length/bond angle/dihedral angle). Real molecule may not follow the reaction path calculated by PES scan. Therefore, care must be taken to attribute chemical and physical significance to them.

APPENDIX VIII

Clusters of Ammonia Borane Complexes

Ammonia borane complexes have recently drawn considerable attention due to their potential application as high-density hydrogen storage system.¹⁻⁵ Dehydrogenation reaction in ammonia borane complexes can occur in the temperature range of 350-410 K. Recent studies indicate that the kinetics of the dehydrogenation reaction can be improved by using silica as catalyst.²

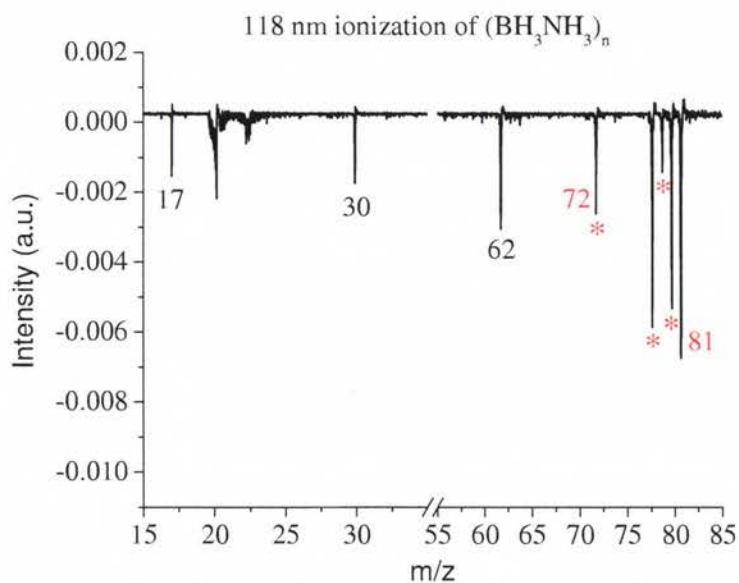


Figure 1: TOFM spectrum of NH_3BH_3 obtained by single photon ionization at 10.5 eV. Mass peaks with * sign are unassigned.

In order to improve the kinetics of hydrogen absorption and desorption in ammonia borane complexes, understanding the geometric and electronic properties that govern the stability, reactivity, and inter- and intramolecular interactions is of paramount importance.⁶ With this in mind, here we have explored gas phase clusters of BH_3NH_3 . BH_3NH_3 has a vapor pressure of 6 Torr at room temperature. Therefore, it is heated to 50°C to obtain enough vapor pressure and gas phase NH_3BH_3 molecules are entrained in molecular beam using a He carrier gas. The clusters of BH_3NH_3 are ionized using single photon ionization at 10.5 eV. Figure 1 illustrates the TOFM spectrum of the BH_3NH_3 clusters.

The above mass spectrum clearly indicates several important mass speaks such as NH_3 at 17 amu, NH_3BH_2 at 30 amu, $(\text{NH}_3\text{BH}_3)_2$ at 62 amu, borazine at 81 amu. NH_3 , NH_3BH_3 , and borazine are generated due to thermolysis of BH_2NH_3 . These peaks are contributed by only the ^{11}B isotope. Boron has two isotopes: ^{11}B with 80% abundance and ^{10}B with 20% abundance. The TOFM spectrum in Figure 1 does not show any peak contributed by ^{10}B isotope. Absence of TOFM peak associated with ^{10}B clearly warrant further study. Nonetheless, a number of observations are interesting here. The only cluster peak observed in the TOFM spectrum corresponds to the dimer of NH_3BH_3 ; no other higher cluster of NH_3BH_3 is found. This result indicates that BH_3NH_3 has a natural tendency to form a dimer. The dimer of NH_3BH_3 possesses unusual dihydrogen bonds which are indicated in Figure 2.

Exploration of structure and electronic properties of ammonia borane complexes can lead to development of next generation high density hydrogen fuel system. Study of their clusters in gas phase, which has not been reported thus far, and is presented in this

appendix, can be an important aid to the effort of understanding structure and dynamics of ammonia borane complexes with respect to their capability of storing hydrogen at the fundamental level.

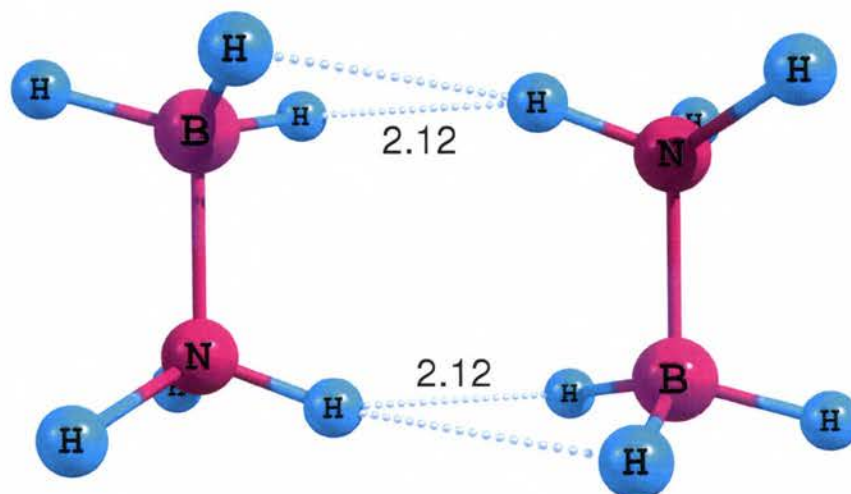


Figure 2: Optimized structure of $(\text{NH}_3\text{BH}_3)_2$ at MP2/6-31G(d) level of theory.

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